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⑥ A MASS-SPECTROMETRIC INVESTIGATION OF THE CHEMISTRY OF
ADVANCED COMPOSITE AND DOUBLE BASE PROPELLANTS,

③

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APPENDIX I

A Mass-Spectrometric Investigation of the Chemistry
of Plateau Burning Propellants

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I. INTRODUCTION

This Annual Summary Report presents the results of a mass spectrometric study of several advanced propellants to determine the chemistry and kinetics of their decomposition. The technical program during this past year involved three propellant groups: (1) minimum smoke composite and HMX formulations containing approximately 1% each of lead oxide and carbon black;* a smokeless double base propellant containing Pb_2O_3 and carbon black;** (2) advanced lead additive formulations;*** and (3) RDX propellant.*** This laboratory's specially designed and constructed dual vacuum chamber and four-stage differentially pumped molecular beam mass spectrometer systems were employed for these studies.

The results obtained for the propellants containing lead oxide and carbon black additives indicated that the carbon reacted with the Pb_3O_4 to produce CO and elemental lead, which vaporized at fairly low temperatures (1000 K) and then reacted with the composite and nitrate ingredients. The propellant containing composite mixtures of ammonium nitrate and ammonium perchlorate produced relatively high intensities of NO_3 . Gaseous lead compounds including $PbCl$, $PbClO$ and $PbNO_2$ were observed as well as $PbNO_3$. These were all intermediate short-lived species and not steady-state combustion flame products. The Allegany Ballistics Laboratory Chaparral Missile Air Defense System candidate propellant, FZO, containing Pb_2O_3 and carbon black was also investigated. The intermediate species $PbNO_2$ and PbO were observed.

Advanced propellant compositions have been formulated at the Naval Ordnance Station, Indian Head, Maryland, which contain lead and copper organic ingredients and samples of several of these were obtained for study. The first phase concerned decomposition of the lead chelate

*Propellant samples obtained from Thiokol/Wasatch Division, Brigham City, Utah, Dr. Michael W. Barnes.

**Propellant samples obtained from Hercules Incorporated, Allegany Ballistics Laboratory, Cumberland, Maryland, Dr. T. F. Comfort.

***Propellant samples obtained from Naval Ordnance Station, Indian Head, Maryland, Dr. A. T. Camp.

of Uvinul 400 from room temperature to above 1000 C. The chelate was found to be very stable, with no measurable decomposition below 400 C. Since no organic hydrocarbons were observed it would appear that the mechanism for decomposition is one of stripping the benzene ring components and the degeneration of the ring to solid carbon, with the lead remaining behind in solid or liquid form, depending upon the temperature.

A significant result of the RDX propellant studies was that the mass spectrometer disclosed that the RDX molecular ring initially splits into two fragments at 148 amu ($C_2N_4O_4H_4$) and 74 amu ($CN_2O_2H_2$). Further decomposition of these major fragments confirmed the previously observed products, including CO , CH_2O , CH_2N_4 , N_2O , NO_2 , and $C_2H_4N_2$.

II. EXPERIMENTAL APPARATUS AND PROCEDURES

The investigations were conducted in two different experimental systems. The decomposition studies were performed in this laboratory's dual vacuum chamber-mass spectrometer apparatus. This system and the experimental procedures have been described previously.¹⁻⁴ Effusion cells were of alumina, with orifices of 1 mm diameter and 6.6 mm thickness. The cells had an inside diameter of 6.6 mm and a length of 25 mm. The ion intensities were determined from their masses, isotopic distribution, and appearance potentials. Only the shutterable (i.e., chopped) portion of the ion intensities was directly recorded. Ion intensities used for equilibrium calculations were obtained with ionizing electrons 2 eV above their appearance potentials.

The combustion studies were conducted in the specially designed four-stage differentially pumped spectrometer system. Complete details of the procedures and methods of calculation have been previously presented.⁴⁻⁹ A molecular beam of frozen species formed in the flame at atmospheric pressure was sampled in the mass spectrometer at 10^{-9} atm pressure.

III. RESULTS AND DISCUSSION

Three groups of propellants and propellant constituents were investigated: (1) composite propellants containing NH_4ClO_4 and

NH_4NO_3 as well as HMX propellants containing both lead oxide and carbon black additives; (2) advanced propellant formulations with lead chelate additives providing high temperature stability; and (3) RDX propellant.

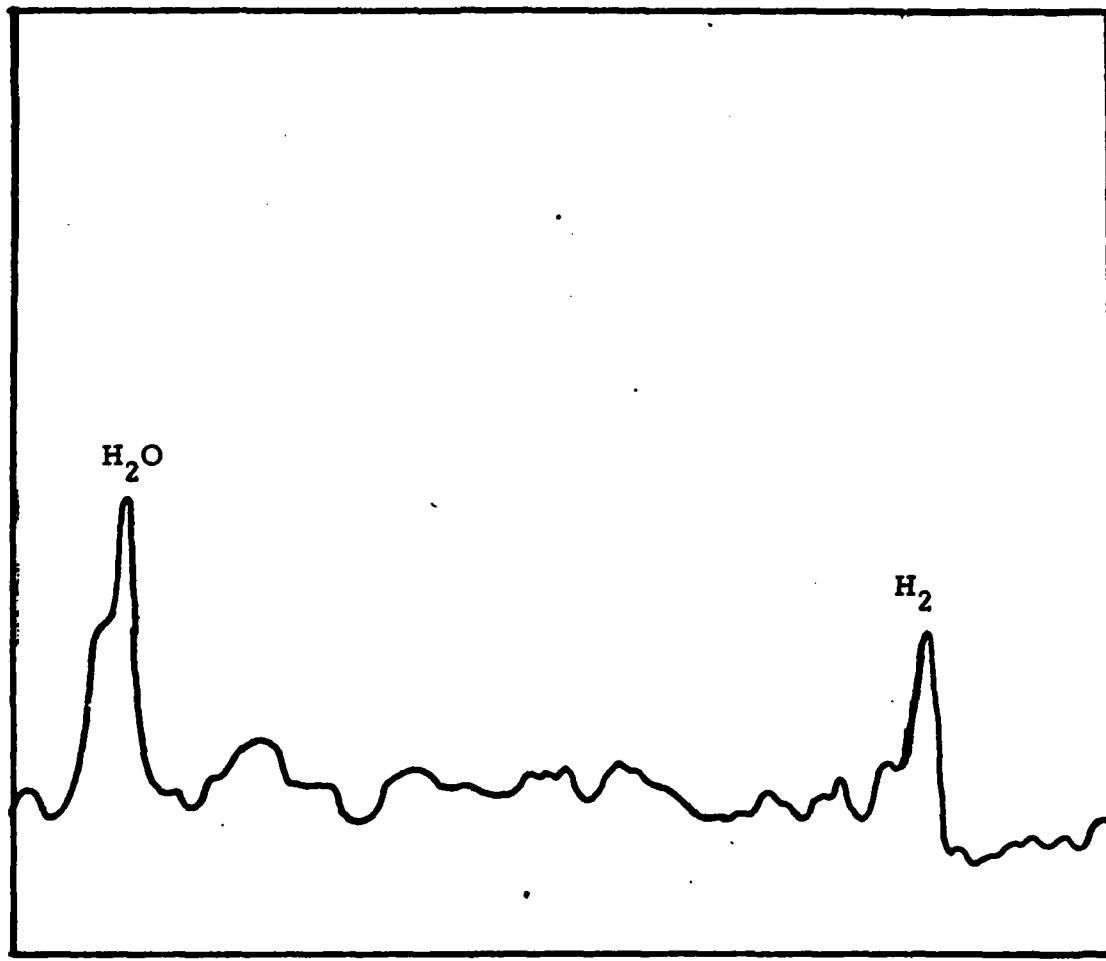
A. Minimum Smoke Propellants N1016, N1010 and N1013

Four minimum smoke propellant formulations containing perchlorate and nitrate composites as well as HMX from Thiokol were studied, each with 1% Pb_3O_4 and 1% solid carbon except for one of the N1010 propellants, which contained only 0.25% C. The N1016 was a composite of NH_4ClO_4 , NH_4NO_3 and HMX, while N1013 contained HMX and ammonium perchlorate only. The N1010 propellant was basically an HMX formulation.

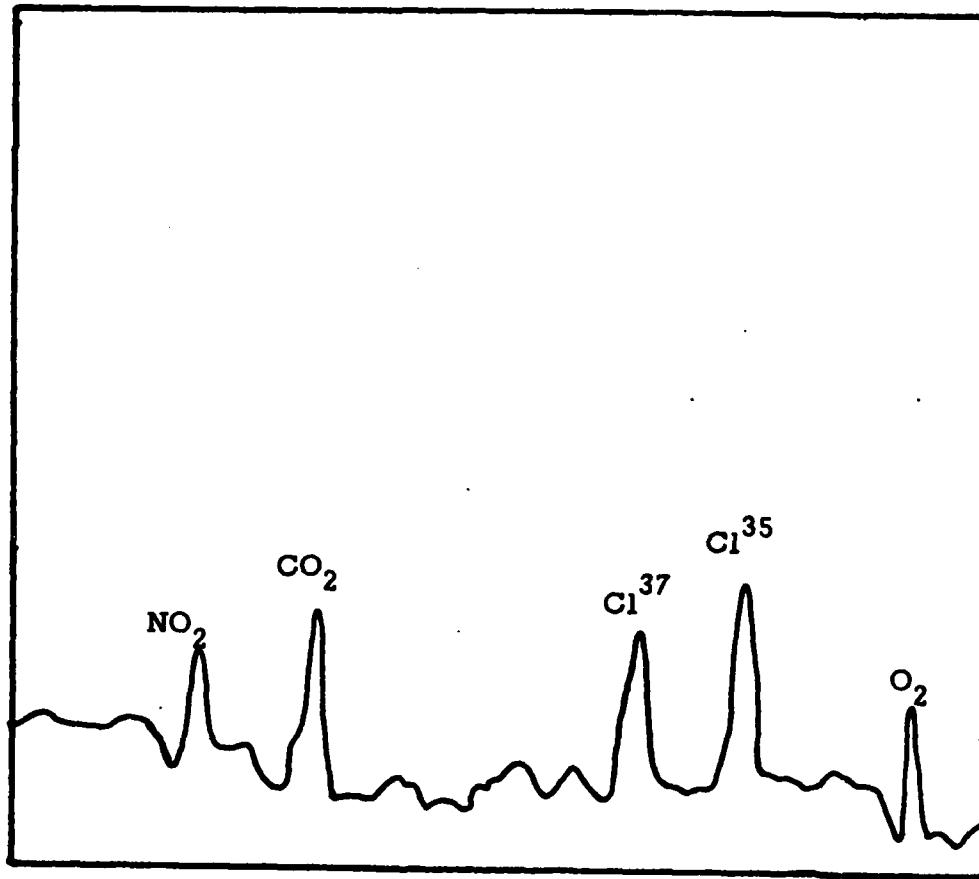
As in previous studies,¹⁰ the mass spectrometer was set at a given mass range to receive the species leaving the propellant after ignition. The propellant sample was placed in an effusion cell that was heated gradually until ignition occurred. The time-of-flight of a species within the quadrupole section is in the microsecond range. In previous studies at this laboratory species produced from electron bombardment were measured at times of less than 100 ns (10^{-7} s).¹¹ Thus the initial products formed in the propellant reaction can be identified if they effuse into the molecular beam to the mass spectrometer. Also, intermediate species having a short lifetime (on the order of milliseconds) would be receivable at the mass spectrometer.

1. N1016 Propellant Investigations

The N1016 propellant decomposition at ignition was investigated in various mass ranges. In the low mass range, as shown in Fig. 1, H_2 and H_2O were produced. In the 30 to 50 amu range O_2 , the Cl isotopes, CO_2 , and NO_2 were observed (see Fig. 2). However, in the intermediate mass range of 50 to 65 several very interesting radicals and compounds were identified (Fig. 3). The ClO radical was observed and, for what is believed to be the first time, the NO_3 species was identified at amu 62. To ascertain this species definitively the mass spectrometer was set an amu value of 62 and a fresh sample was ignited. Figure 4 shows the NO_3 species with a significant intensity. In the previous studies involving the plateau double base propellants



**Fig. 1. Species produced at ignition of Thiokol Propellant N1016
in the 1 - 20 amu range**



**Fig. 2. Species produced at ignition of Thiokol Propellant N1016
in the 30 - 50 amu range**

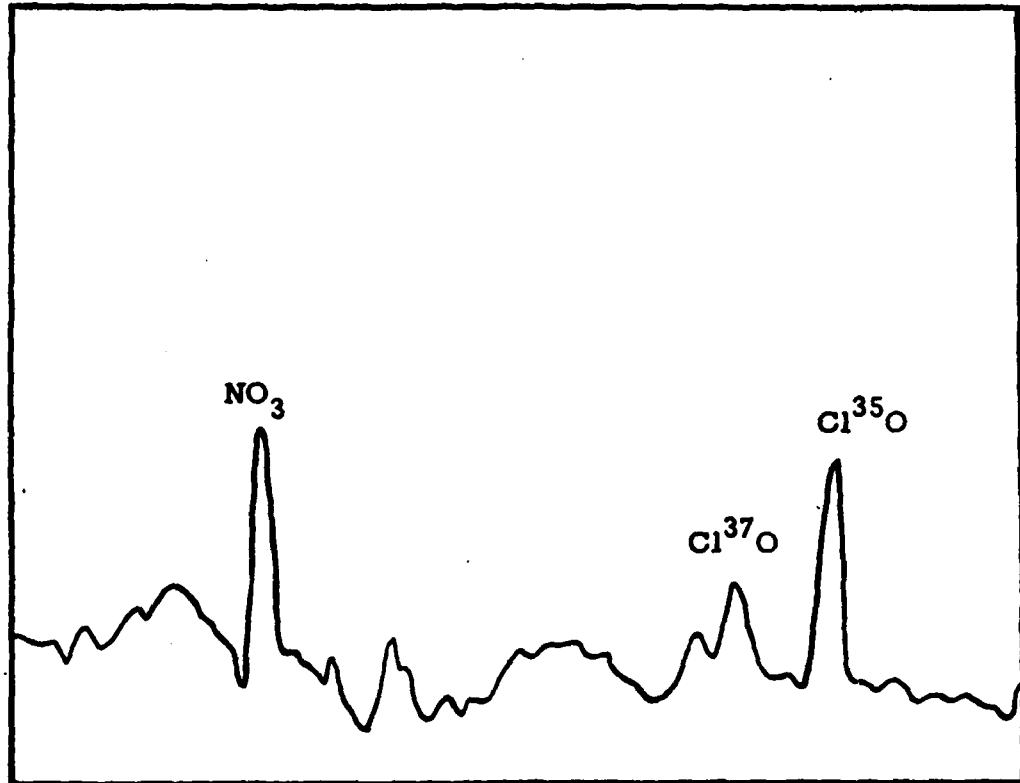


Fig. 3. Species produced at ignition of Thiokol Propellant N 1016
in the 50 - 65 amu range

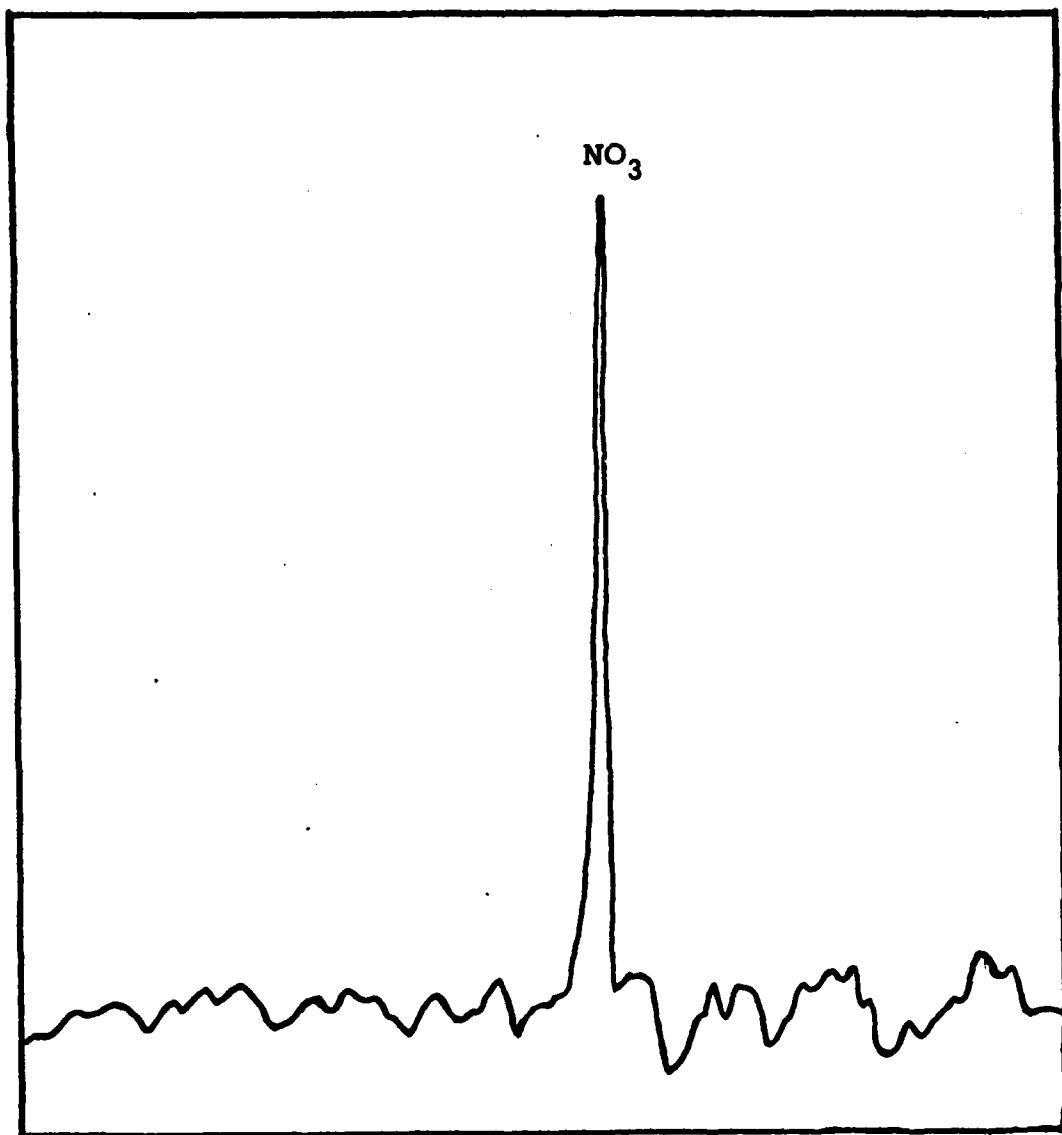
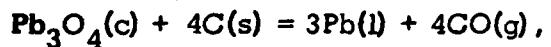


Fig. 4. NO_3 species at ignition of Thiokol Propellant N1016
at 62 amu

no NO_3 was observed, which indicated that the NO_2 groups, and not the NO_3 species, were released upon the nitrate ester decomposition. However, Dauerman and Tajima¹² assumed that the lead additive caused an increase in NO_3 concentration although NO_3 was not directly observed. NO_3 has been reported to have a short half-life of approximately 3 seconds.¹³ Our previous studies on the double base propellants¹⁰ indicate that the cleavage of the CONO_2 bonding results in CO and NO_2 . The C-O bond is much stronger than the N-O bond. The appearance of NO_3 from the Thiokol propellant studies indicates that the mode of decomposition of ammonium nitrate produces NO_3 . The ClO radical results from the ammonium perchlorate decomposition.

The reaction between Pb_3O_4 and carbon to produce the lead atom along with CO is extremely exothermic. This reaction,



has a free energy of -446.8 kJ at 1000 K. The lead compounds identified included PbCl , PbClO and PbNO_2 , as shown in Fig. 5. The PbCl and PbClO species are a result of the decomposition of ammonium perchlorate as observed in the lower atomic weight spectra (Fig. 3).

Since NO_3 radicals were found to be present the mass spectrometer was set to receive species corresponding to PbNO_3 at an amu of 269. As can be seen from Fig. 6, a large amount of this species was formed. These results support the mechanisms of intermediate lead compound formation for super-rate and plateau burning propellants. The Pb atoms react with the Cl , ClO , NO_2 and NO_3 radicals released upon initial decomposition from the salts and accelerate their decomposition, resulting in super-rate burning.

2. N1010 Propellant Investigations

The ignition study on the two N1010 propellants containing HMX as the oxidizer did not show the formation of NO_3 as in the case of the AN propellant. These results were similar to those obtained with the double base propellants, and tend to support our contention that the nitrate esters decompose via bond breaking to CO .

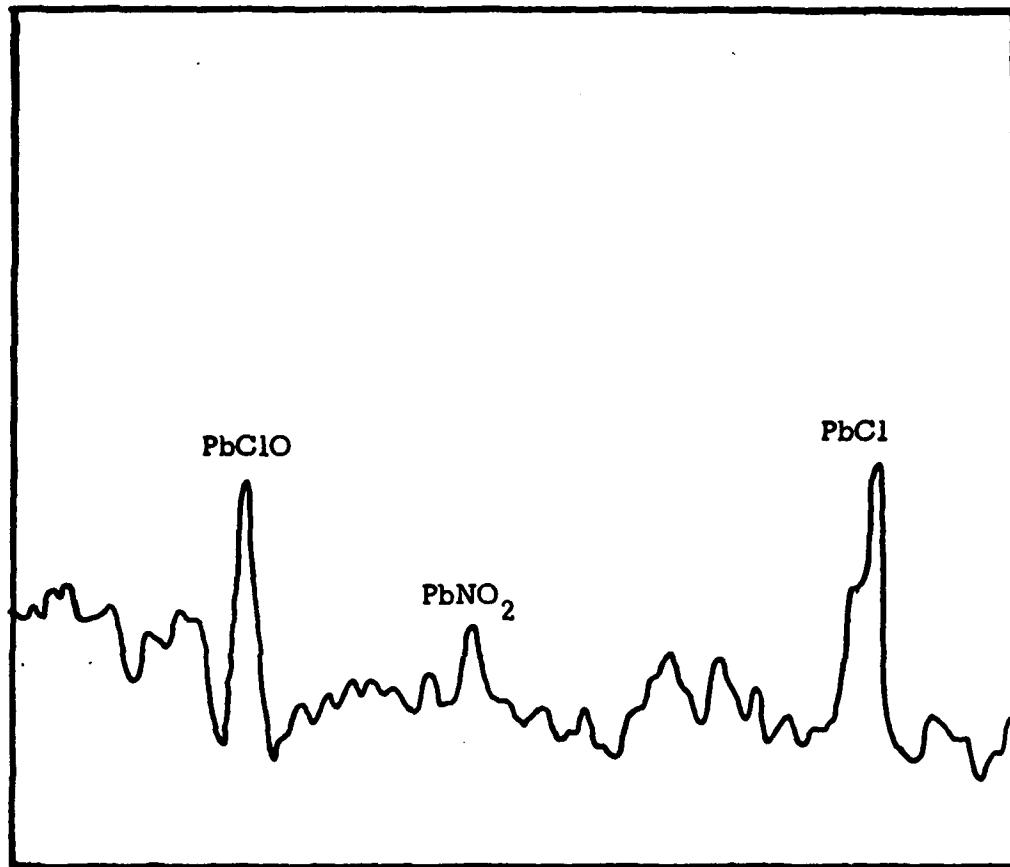


Fig. 5. Lead species produced at ignition of the Thiokol Propellant N1016 at ignition. The amu range was 240 to 275.

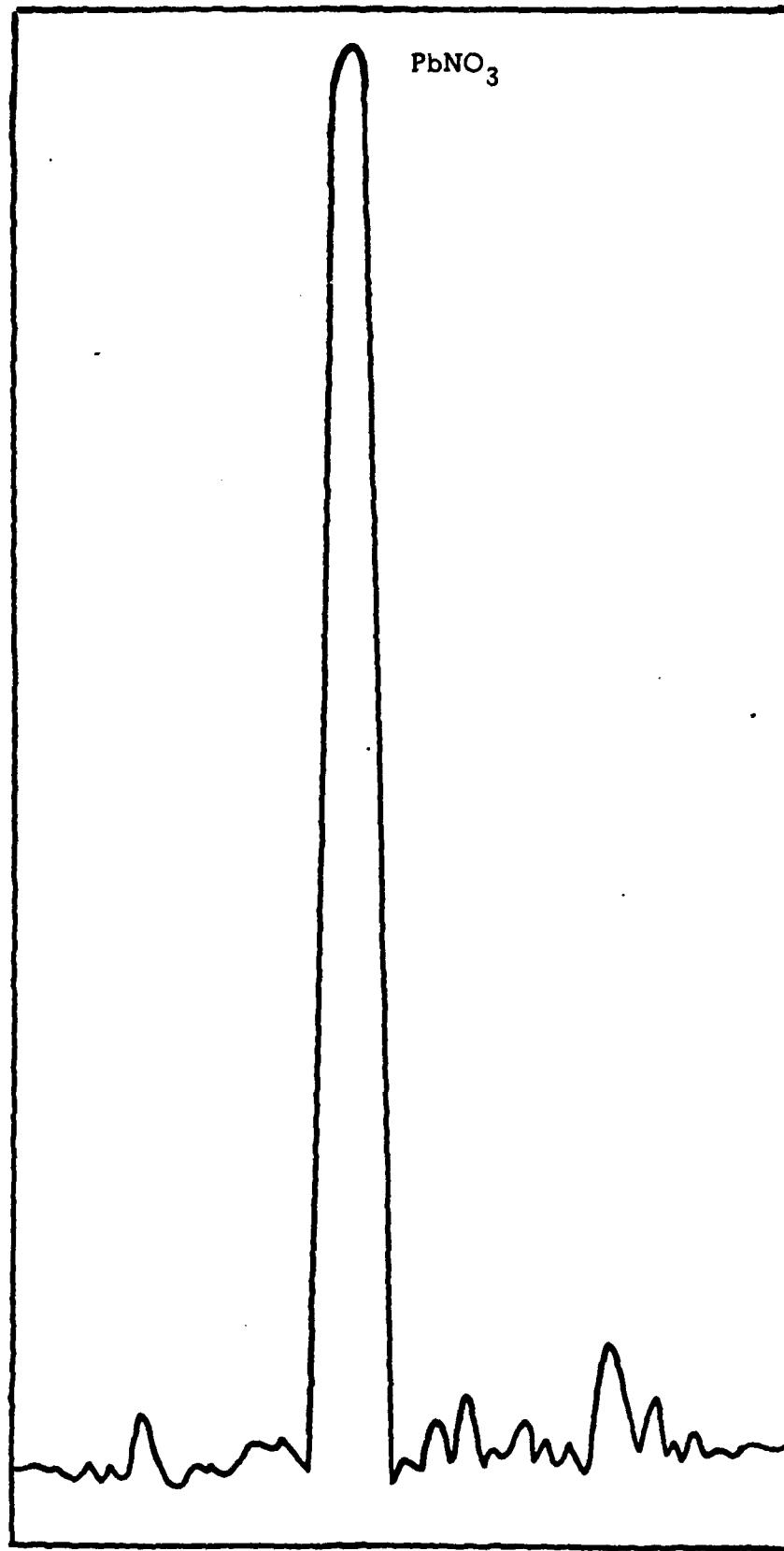


Fig. 6. PbNO_3 Species Produced at Ignition of
Thiokol Propellant N1016

and NO_2 groups, and not to NO_3 as suggested by Dauerman and Tajima¹² and by Chameides and Walker.¹³ The two N1010 samples had identical compositions with the exception that one contained 1% solid carbon while the other contained only 0.25% carbon, as mentioned previously. The products of the low amu range for the two propellants were identical (H_2 , H_2O , CO , N_2 , NO , O_2 , CO_2 and NO_2). In the amu range 1 to 20 only H_2 and H_2O were observed in significant amounts, as shown in Fig. 1. Figure 7 shows species in the 26 to 50 amu range arriving at the mass spectrometer after ignition. In the high mass range the products observed were similar to those obtained from ignition of the lead additive double base propellants. Figure 8 shows Pb and PbNO_2 peaks of nearly equal concentration. The sample containing only 0.25% C also shows these two peaks, with a slightly lesser quantity of PbNO_2 (Fig. 9). However, it should be emphasized that these peak heights are not quantitative and may vary with each mass spectrometer sampling. The decomposition of these two propellants appears to follow the reduction of the Pb_3O_4 with carbon to lead atoms.

3. N1013 Propellant Investigations

The Thiokol N1013 propellant contained both HMX and ammonium perchlorate. The high temperature species produced on ignition were similar to those of Propellant N1010, with the addition of strong PbCl peaks, as shown in Fig. 10.

B. FZO Propellant Investigations

This propellant was developed at the Allegany Ballistics Laboratory under the auspices of the U. S. Army Missile Research and Development Command for a smokeless rocket motor for the Chaparral Missile Air Defense.¹⁴ The FZO is a double-base formulation containing Pb_2O_3 and carbon black.

Figures 11, 12 and 13, which are illustrative of these studies, show the gaseous species produced at ignition in the amu range 10 to 20 (Fig. 11), 27 to 50 (Fig. 12), and 200 to 300 (Fig. 13). The ignition species in Fig. 11 show strong OH and H_2O peaks, with a fairly small CH_2 peak at amu 14. The peaks appearing as intermediates prior to complete combustion of the CHNO compositions were apparent

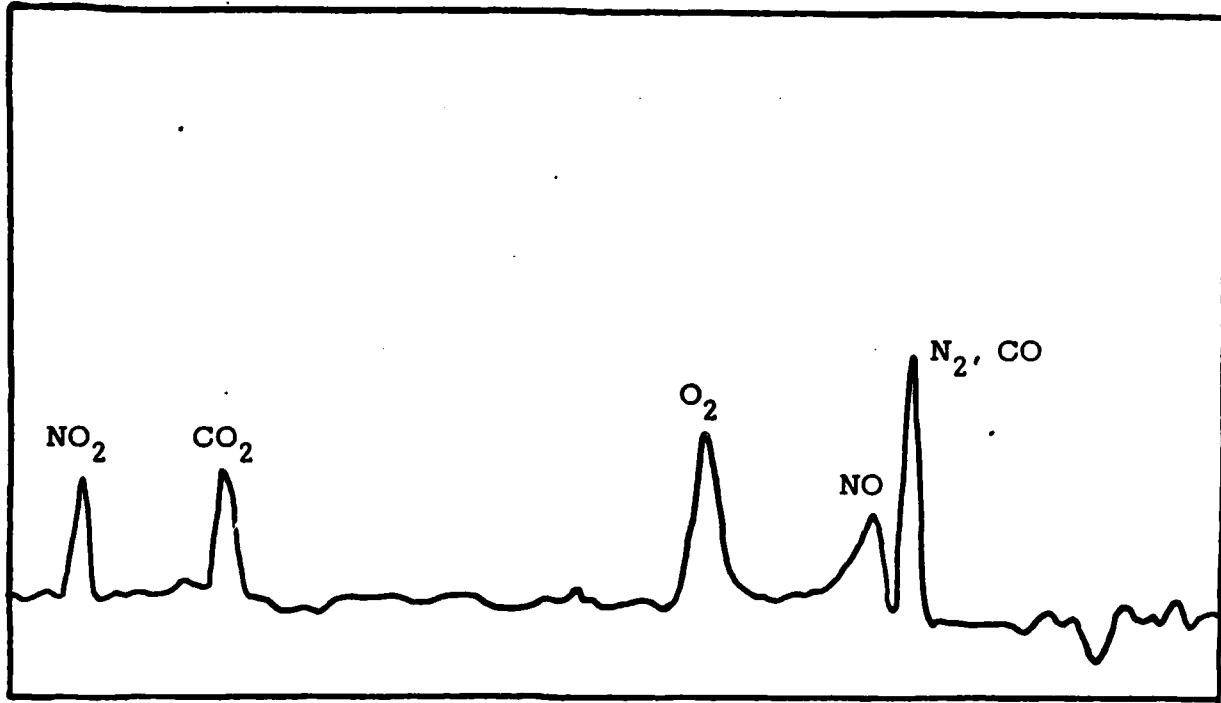


Fig. 7. Species Produced at Ignition of Thiokol Propellant N1010
in the 26 - 50 amu range

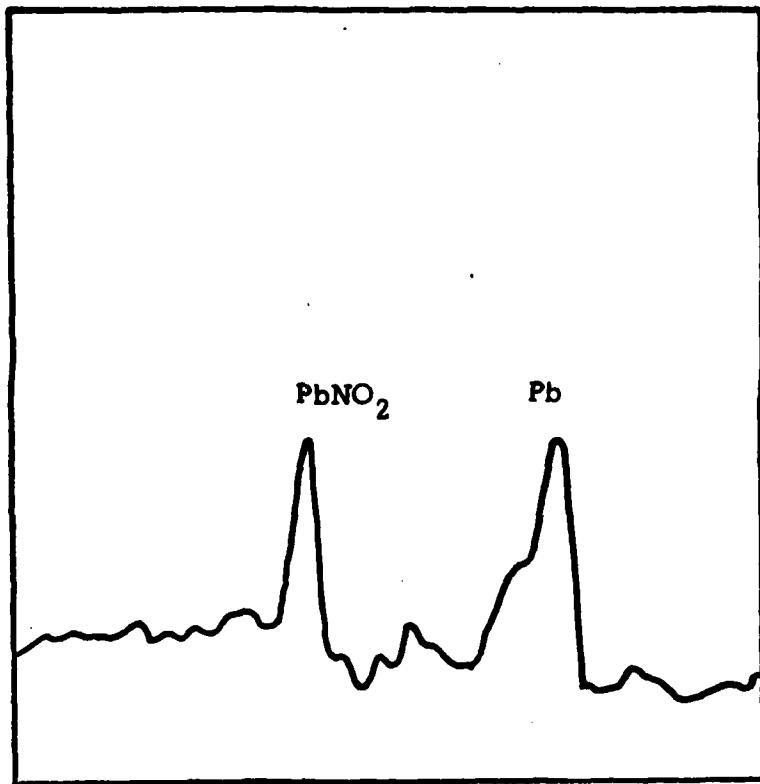


Fig. 8. Species Produced at Ignition of
Thiokol Propellant N1010 in the 200 - 300
amu range

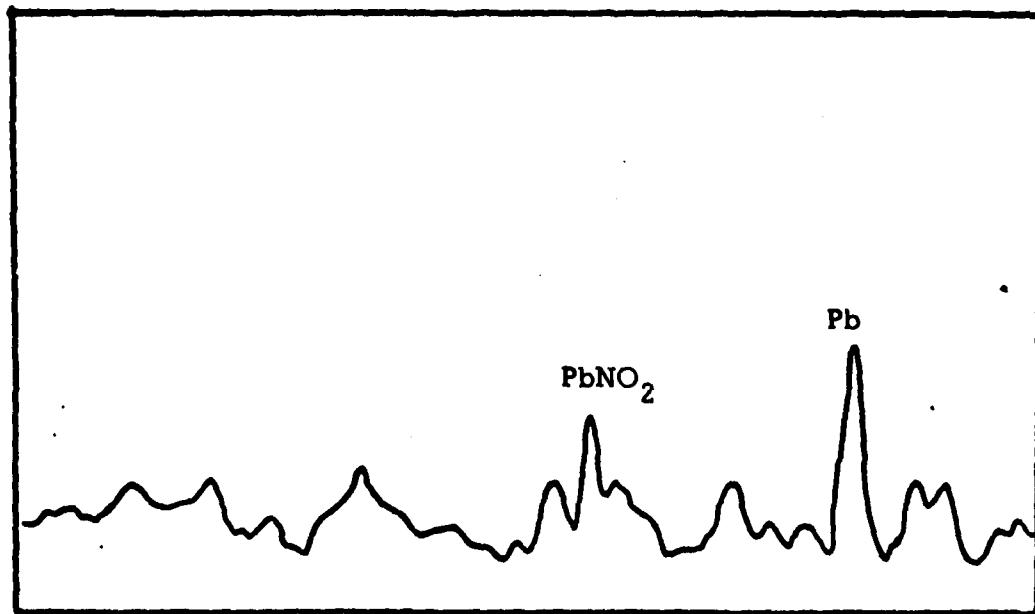


Fig. 9. Species Produced at Ignition of Thiokol Propellant N1010
with 0.25% C in the 200 - 300 amu range

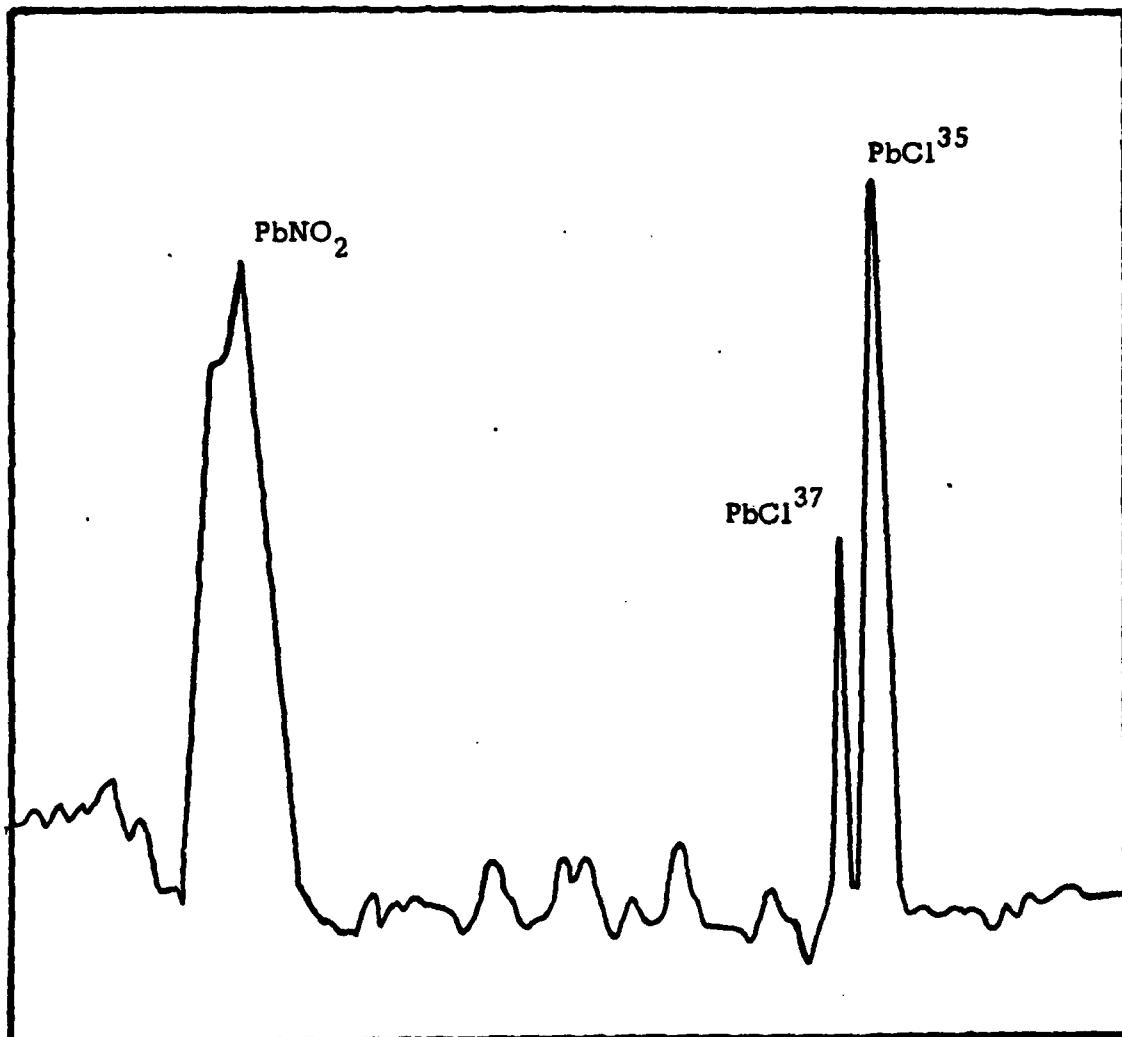


Fig. 10. Species Produced at Ignition of Thiokol Propellant N1013
in the 240 - 260 amu range

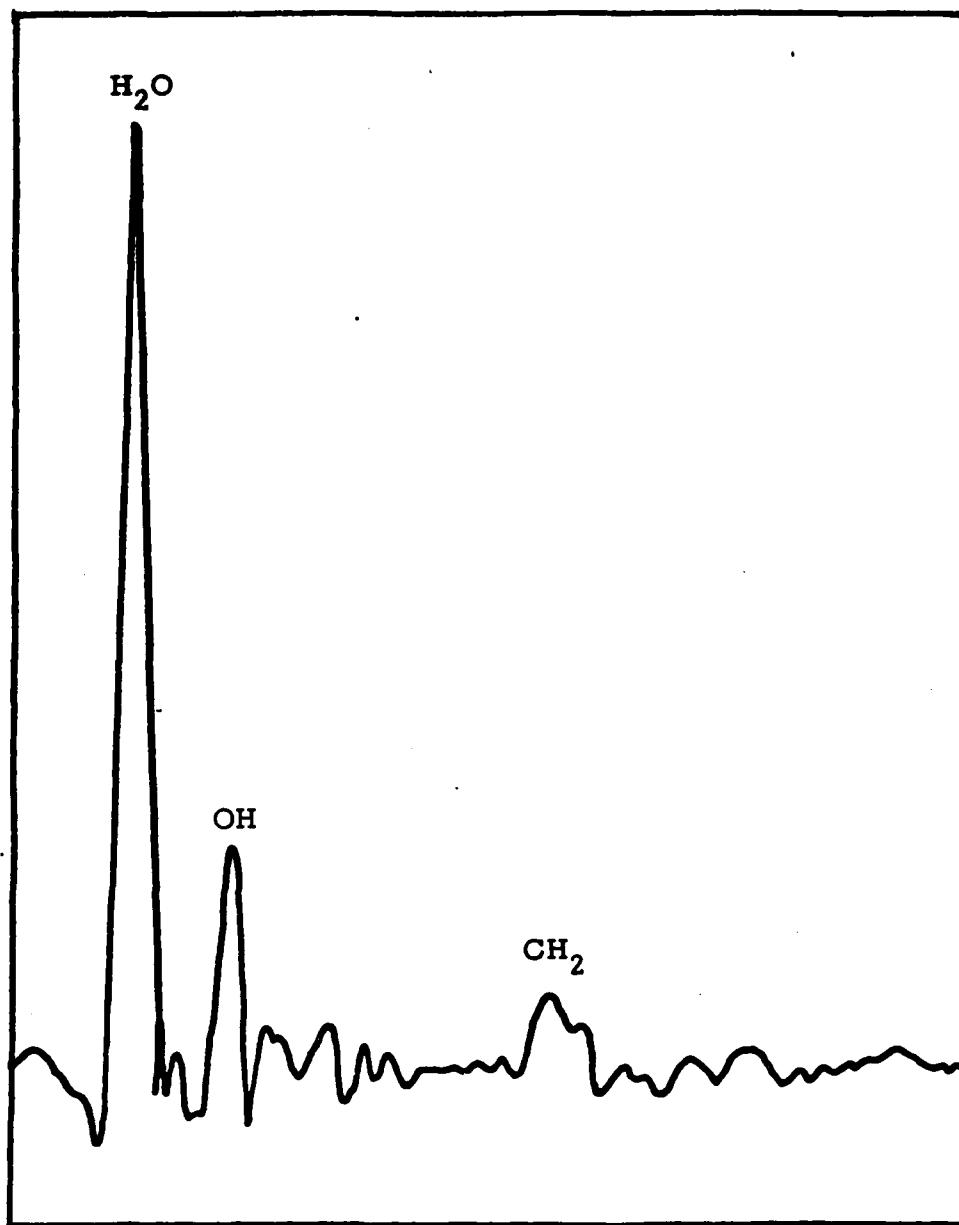


Figure 11. Species produced at ignition of the FZO propellant in the 10 - 20 amu range

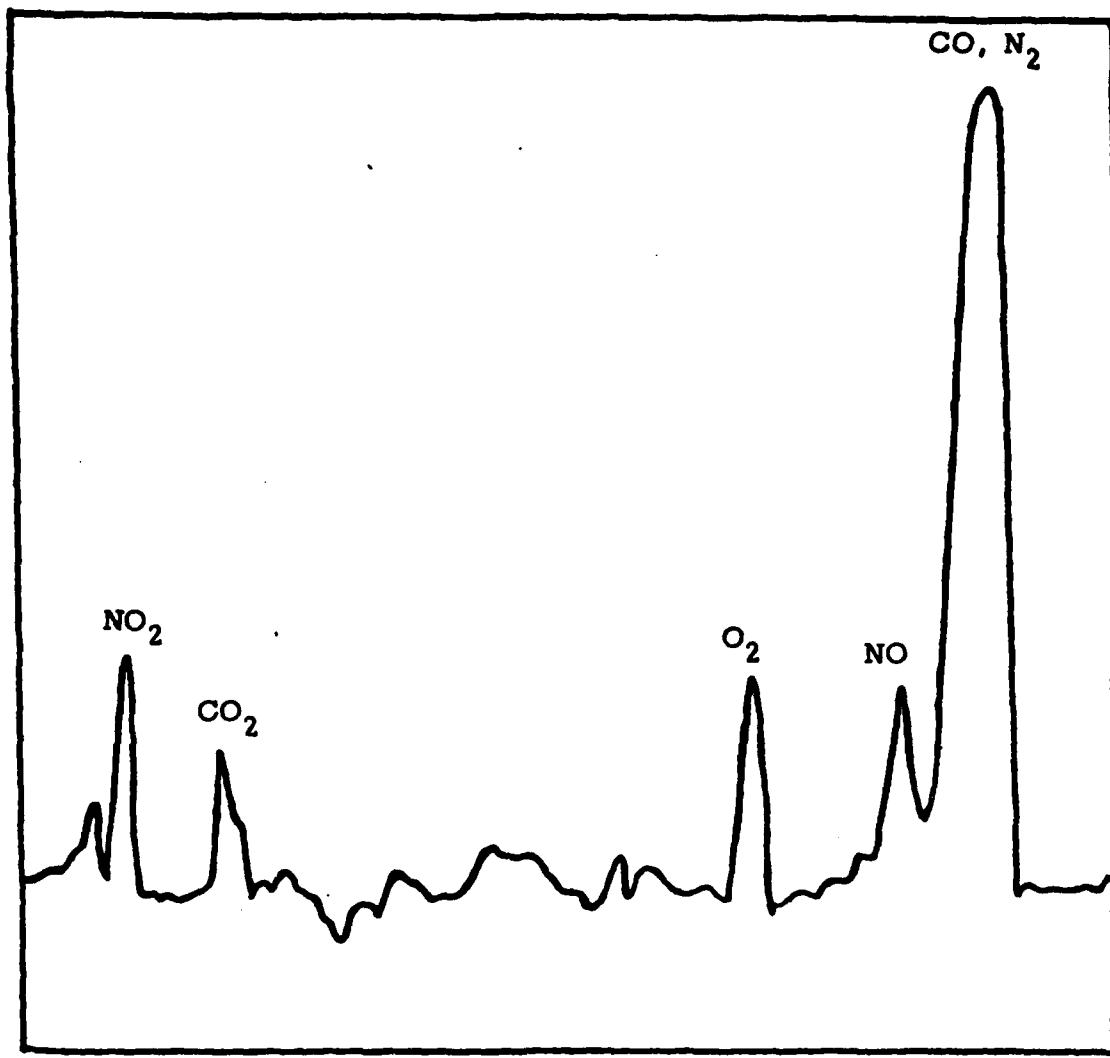


Figure 12. Species produced at ignition of the FZO propellant
in the 27 - 50 amu range

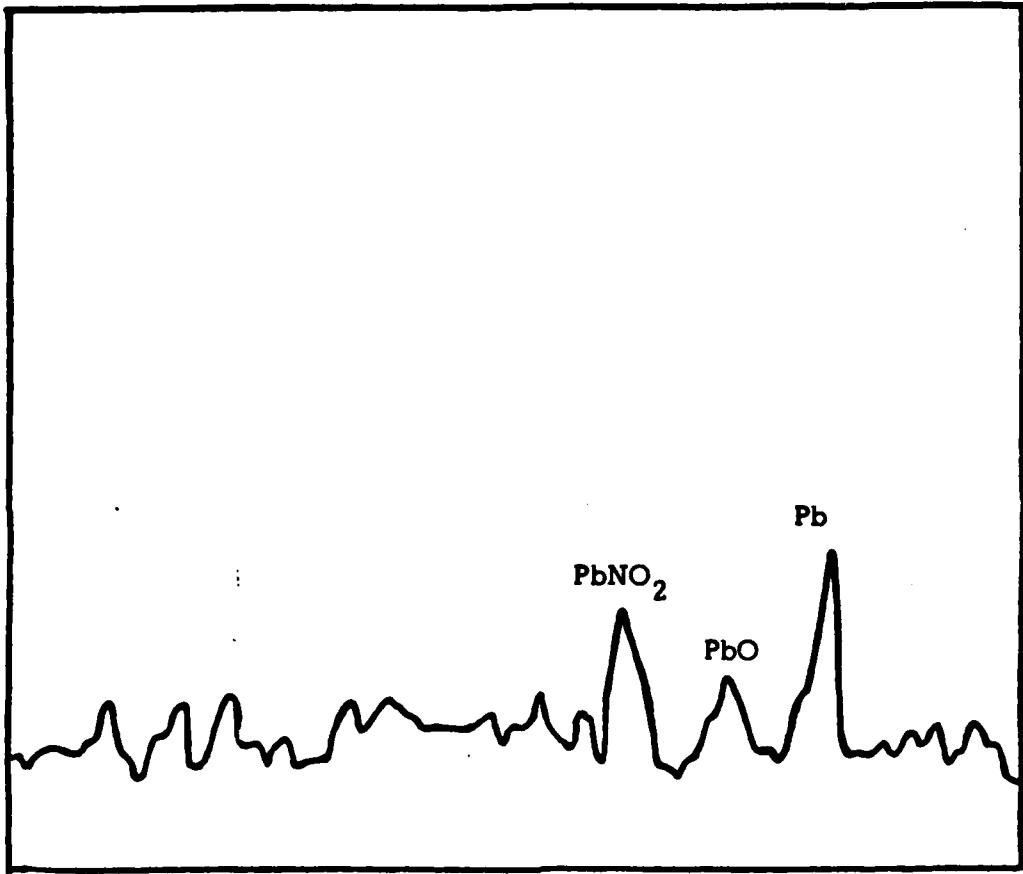
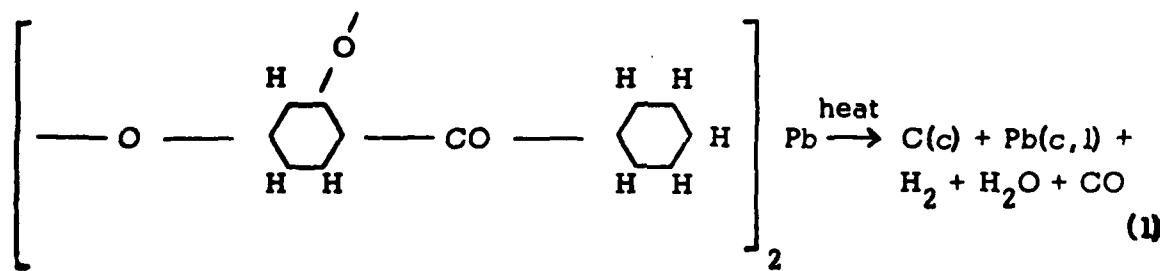


Figure 13. Species produced at ignition of the FZO propellant in the 200 - 300 amu range

CO, N₂, NO, O₂, CO₂ and NO₂ (Fig. 12). Of particular interest was the appearance of a strong NO₂ peak at amu 46, leading to the formation of PbNO₂, as was found in the previous double-base lead modified propellant studies. Figure 13 shows the PbNO₂ peak in approximately the same concentration as metallic lead. A PbO peak at amu 223 was also observed. This is not unexpected since the propellant contains insufficient carbon to reduce the entire amount of lead oxide to elemental lead. Thus the compound Pb₂O₃ will decompose upon heating to the lower lead oxides, including the gaseous suboxide PbO, which was observed.

C. Decomposition Studies of Uvinul 400

The Naval Ordnance Station is developing a family of advanced smokeless propellants with high burning rates. These contain copper and lead organic chelates as additives. The first additive to be investigated was the lead chelate of Uvinul 400, the designation for 2,4-di-hydroxybenzophenone. Decomposition studies were performed from room temperature to above 1000 C. The chelate was found to be very stable, with no observed decomposition below 400 C. At 400 C decomposition commenced and vapor species were detected with the mass spectrometer. Figure 14 is a typical spectrum of the vapor species arriving at the mass spectrometer. At 425 C only H₂, H₂O and CO were observed. No other vapor species appeared until gaseous Pb was seen at about 700 C. The approximate concentration of Pb atoms at 825 C can be seen in Fig. 14. Since no organic hydrocarbons were observed, the mechanism for decomposition appears to be one of stripping the benzene ring components and the degeneration of the ring to solid carbon.



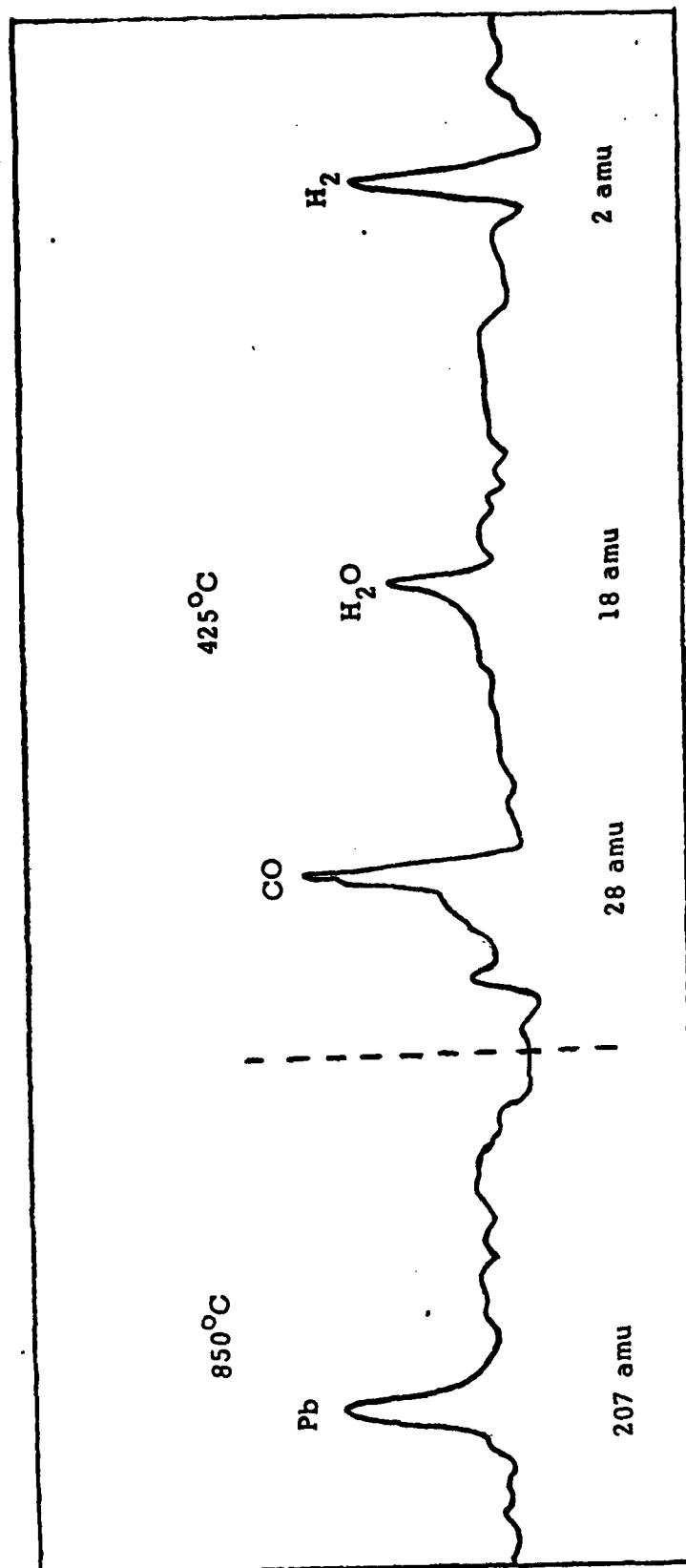


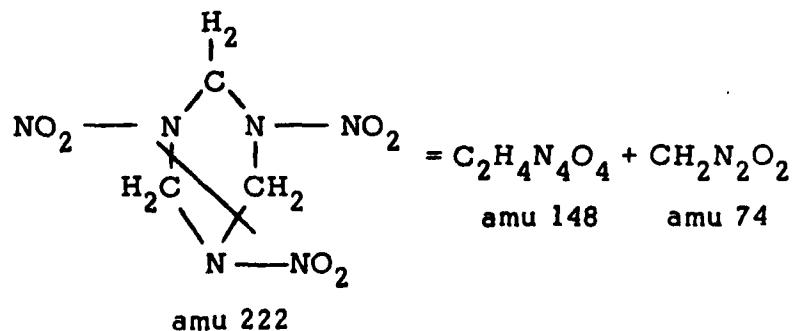
Figure 14. The Decomposition of the Lead Chelate of Uvinul 400

The lead remains behind in solid or liquid form, depending upon the temperature. Quantitative data were taken to further check these observations. Samples of the chelate were heated in vacuum at a temperature of 425 C for 5 hours. The weight loss corresponded to 35% of the original weight. The theoretical weight loss based upon equation (1) is 37%. Therefore, it can be concluded that, as mentioned previously, decomposition of the lead chelate is a stripping of the ring components and a collapsing of the ring to carbon and lead, which remains behind.

D. Decomposition Studies on RDX

Since the use of RDX instead of double base constituents may improve propellant performance, an investigation of the combustion characteristics of RDX was initiated prior to the study of propellant combustion characteristics. Decomposition of this compound has been investigated previously. The results appear to be somewhat controversial. Rauch and Fanelli¹⁵ reported that four previous investigations had not reported NO_2 , which they observed in their studies. Bradley, et al,¹⁶ also recently reported the identification of NO_2 with a mass spectrometer. The purpose of the investigation at this laboratory was to identify the mode of decomposition and the products employing the mass spectrometer. Mass spectrometric studies were made below and above the melting point of 204.5 C. Figure 15 shows the peaks observed below the melting point, including amu values of 28, 30, 42, 44, 46, 56, 74 and 83. Figure 16 depicts the peaks at amu 28 to 74, and Figure 17 shows peaks appearing in the amu range 82 to 148, all above the melting point, at 220 C.

RDX completely decomposes to gaseous compounds, with no residue remaining behind. It appears that a major mode of decomposition is the splitting of the RDX ring into two major fragments of 148 and 74 amu, as



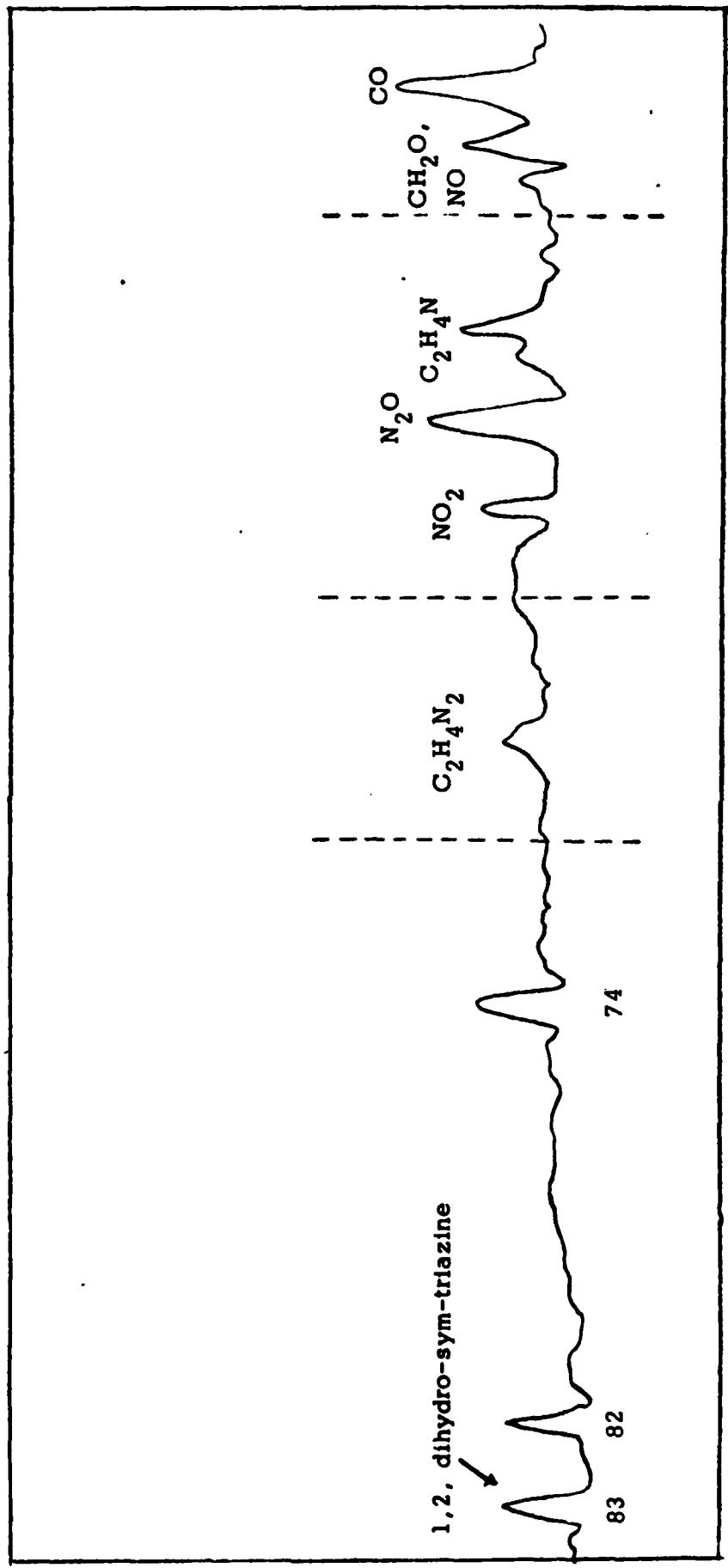


Figure 15. Decomposition of RDX below the Melting Point at 200°C (amu range 28-83)

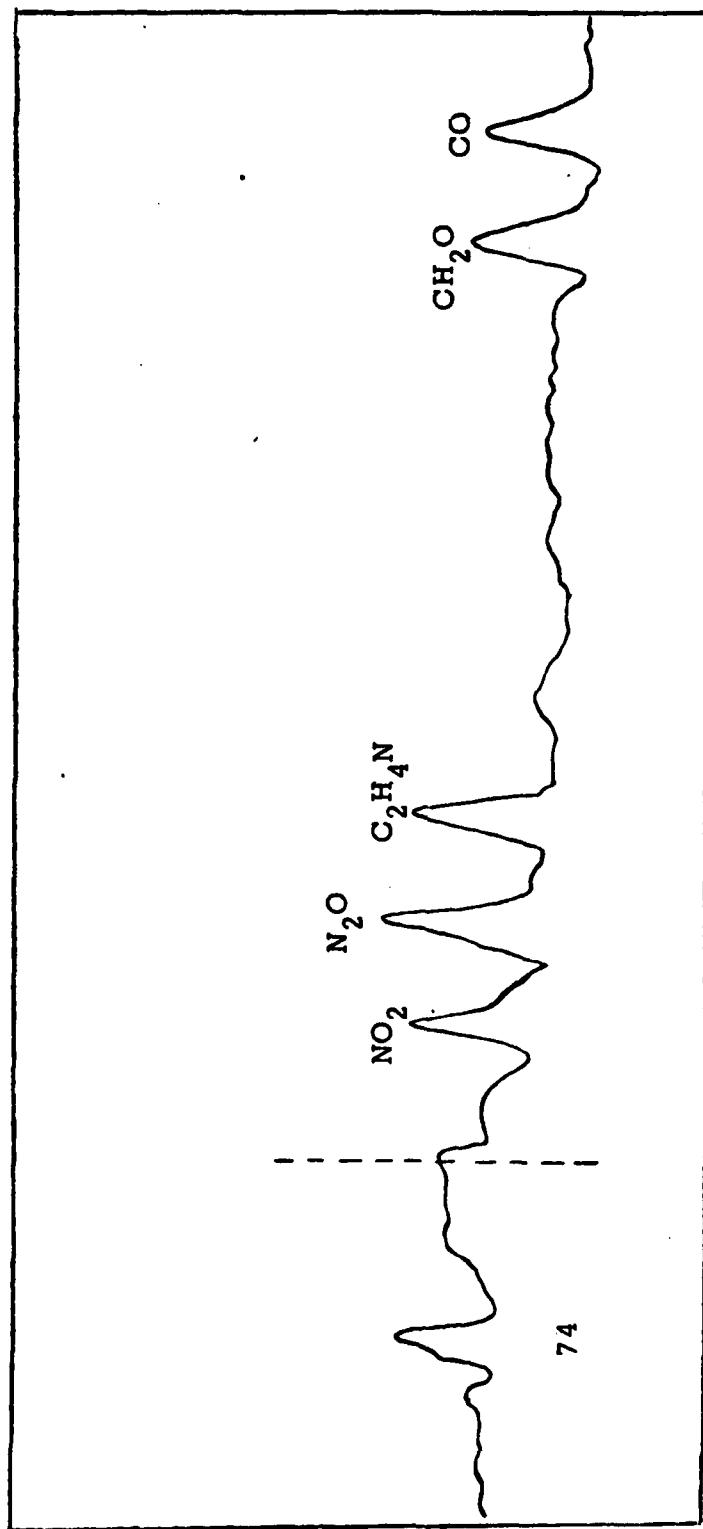


Figure 16. The Decomposition of RDX above the Melting Point at 220°C
(amu range 28 - 74)

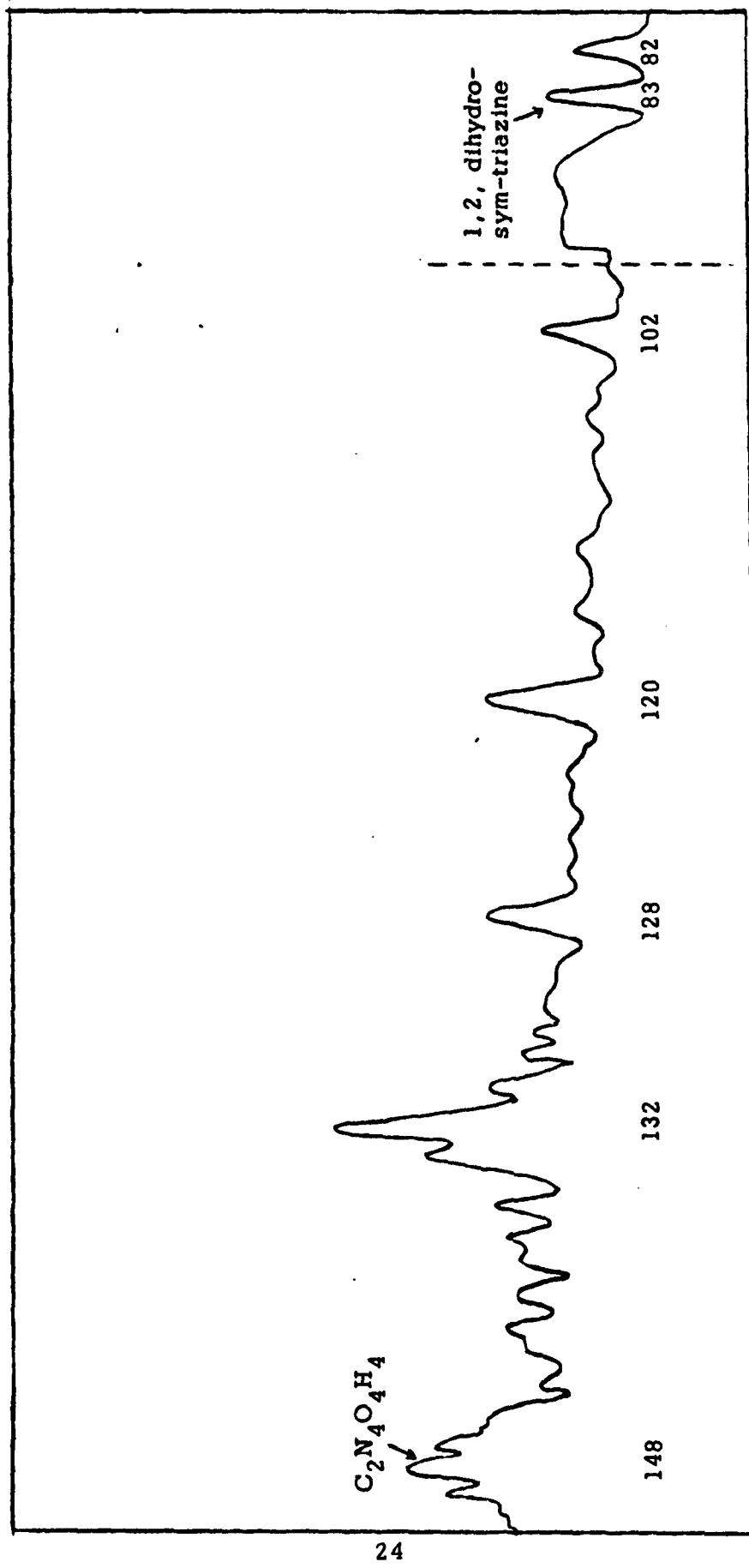
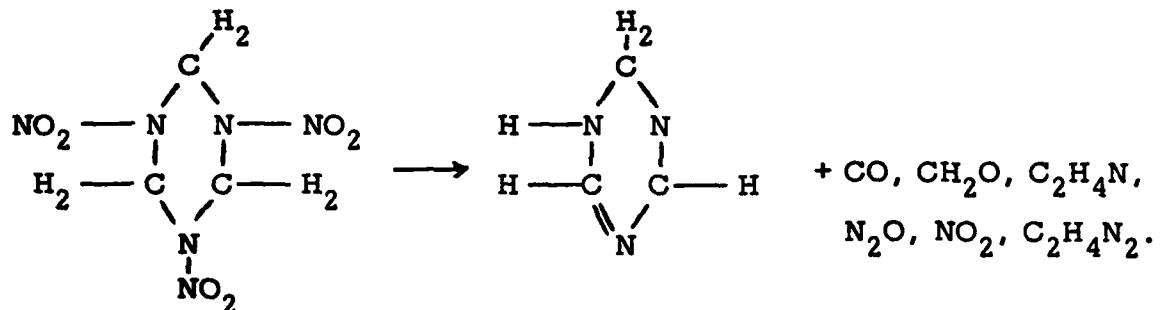


Figure 17. The Decomposition of RDX above the Melting Point at 220°C
(amu range 82 - 148)

Another mode of decomposition, determined from the identification of the 83 amu peak, is the formation of the ring compound, 1,2, dihydro-sym-triazine, as well as a number of low molecular weight molecules.



RDX

1,2,dihydro-sym-triazine

In this decomposition the NO₂ groups are stripped from the RDX. The other decomposition species identified below the melting point were CO at 28 amu, CH₂O and NO at amu 30, C₂H₄N at amu 42, N₂O at amu 44, NO₂ at amu 46, and C₂H₄N₂ at amu 56. Further decomposition results in a 56 amu peak, the removal of two NO₂ groups, a peak at amu 102 resulting from the removal of one NO₂ group, and a peak at amu 132 resulting from the removal of one O atom.

IV. PUBLICATIONS

During this period a publication entitled "A Mass-Spectrometric Investigation of the Chemistry of Plateau Burning Propellants" appeared in Combustion and Flame.¹⁰ This publication is included with this report as Appendix I.

V. SUMMARY AND CONCLUSIONS

Previous studies at this laboratory involving lead organic salt additives allowed several conclusions: (1) stripping of the organic salt frees the lead atom to appear in the condensed and gaseous phases; (2) the reaction of the lead with the nitrate esters increases the burning rate and produces PbNO₂ as an intermediate; and (3) the combustion

products agree with those at equilibrium. Details of these studies are presented in Appendix I. This section summarizes some additional interesting observations and conclusions based upon the results of the recent ignition and decomposition studies.

Although lead oxide in itself would not be a suitable catalyst for accelerated burning, as found by Hewkin, et al,¹⁷ and by Preckel,¹⁸ its reduction to elemental lead in both the condensed and gaseous phases does provide a basis for catalytic action. The reaction between Pb_3O_4 and C is extremely energetic and highly exothermic at relatively low temperatures. As a result, in the investigation of the four Thiokol propellants it was found that numerous lead compounds were formed as intermediates, including $PbNO_2$, $PbNO_3$, $PbCl$ and $PbClO$. These are derived from the Cl and ClO radicals from perchlorate decomposition, NO_3 from nitrate decomposition and NO_2 from nitramine decomposition. The formation of these intermediates accelerated the decomposition of the oxidizing ingredients. In the flame combustion region at temperatures above 2000 K these intermediates further reacted to form the equilibrium products predicted from thermodynamic propellant calculations.

The FZO smokeless propellant also exhibited combustion and ignition characteristics similar to the Thiokol propellants. It has been determined that the lead oxide carbon additives greatly improve the stability and operational characteristics of the FZO propellant.¹⁴ However, since FZO does not have sufficient carbon to completely reduce the Pb_2O_3 , it is not as effective as a modifier for plateau burning.

The first of the Naval Ordnance Station advanced propellant additives to be studied, the lead chelate of Uvinul 400 (2,4-dihydroxybenzophenone), was found to be extremely stable with no observable decomposition below 400 C. Above 400 C the decomposition occurred only by the stripping of the ring components, H_2 , CO and OH. The benzene ring did not vaporize, but decomposed to solid carbon which remained behind with the elemental lead. At temperatures above 700 C elemental Pb was observed.

The decomposition of RDX has been somewhat controversial. A number of investigators did not report the observance of NO_2 , whereas

others did. The current experiments definitely establish that RDX completely vaporizes upon heating without leaving any residue. However, its mode of decomposition appears to be complicated. Our results to date indicate that initially the molecule breaks into two large fragments, with subsequent further decomposition of these into smaller fragments.

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APPENDIX I

A Mass-Spectrometric Investigation of the Chemistry of Plateau Burning Propellants

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A mass-spectrometric study has been conducted involving double-base plateau burning propellants containing lead and copper organic salts. The pyrolysis and combustion of the metallic salts were also investigated. The results revealed that the metallic salts containing oxygen bonding to the metal decompose to the gaseous and condensed phase metallic elements, while covalent salts merely vaporize. The gaseous lead or copper atoms then react with the nitrate esters to form compounds such as $PbNO_2$ and $CuNO_2$, which are stable in the intermediate temperature zones. When the nitrates enter the combustion zone they react to produce the metallic hydroxides and oxides as predicted by the thermodynamic equilibria. The formation of the $PbNO_2$ and $CuNO_2$ may possibly be the criterion for the mechanism of the mesa effect.

INTRODUCTION

This paper presents the results of a mass-spectrometric study of the chemistry of super-rate and plateau burning propellants. Double-base propellants containing lead and copper additives were investigated. Experiments were performed to determine the mechanisms and reactions resulting with addition of organic lead or copper compounds to nitrate ester propellants. The investigation was conducted in three phases: (1) decomposition studies of organic lead and copper additives, (2) combustion studies of the additives in an H_2/O_2 flame, and (3) studies of the reactions of the propellant itself after ignition.

Various experimental studies have been conducted involving lead-compound catalyzed double-base propellants, including investigations concerning heat of explosion, strand burning, rocket motors, and others [1-12]. The reported data indicate that the key to establishing the mechanism for super-rate and plateau burning may lie in the understanding of the reactions taking place between the lead additive and the nitrate ester prior to high-temperature combustion. Thermo-

couples imbedded in the solid propellant below the burning surface have indicated that some types of reactions occur prior to combustion [6], showing a higher temperature for propellants containing lead additives than for the unmodified propellants. In addition, several investigative groups found that the heat of combustion was higher in the case of the lead-additive propellant [2, 5, 6]. This may have been due to either the direct combustion of the lead compound forming higher-energy acidic or oxide compounds or to the combustion of a lead intermediate, resulting in more energetic combustion products.

It has been shown that no plateau is formed when the propellant is burned at high pressures, resulting in higher temperatures. This suggests that at these high temperatures the intermediate compounds that would normally result from the reaction between the lead additive and the ester are not formed; instead, both the lead compound and the nitrate ester are consumed individually and thus no plateau burning occurs [5].

Several hypotheses and theoretical mechanisms have been advanced for super-rate and plateau burning lead-compound additive propellants.

Based on previous investigations, these include: (1) the formation of a complex between the chelate lead atom and alkyl nitrate [6]; (2) radiation absorbed into the propellant from the flame [7]; (3) the reduction of NO by catalysis action of the lead compound acting in conjunction with the carbon on the burning surface [1, 4]; (4) the exothermic reduction of NO_2 to NO with accompanying oxidation of C, H, O species [5]; and (5) the formation of NO_3 [3].

Although these previous investigations offered conclusions regarding the mechanisms involved, no general agreement has been reached and thus the chemical causes of plateau burning have remained unresolved. Specifically, uncertainties and disagreements exist pertaining to the mechanisms that produce plateau burning when lead compounds are added to double-base propellants, the identification of the preflame products involving the lead and double-base components, and the lead-compound combustion products.

BACKGROUND

Early work on the use of metal additives to produce super-rate and plateau burning has been reported by Preckel [1], who found that the addition of certain lead compounds to nitrocellulose propellants tended to limit the burning rate at pressure levels below 5000 psi. Plateaus were formed at lead stannate concentrations of 0.5-1%. Higher lead-salt concentrations moved the plateau to lower pressures and burning rates. He found that aliphatic lead salts resulted in plateau burning at low pressures with low burning rates, while aromatic lead salts gave plateau burning at high pressures with high burning rates.

Lenchitz and Haywood [2] studied photographically the burning surfaces of double-base propellant strands modified with lead additives. They found that at burning pressures of 150 lb/in² the burning surface of the modified propellant was homogeneous, was well formed, and had a uniform glow. The nonmodified propellant surface showed localized pockets of reaction, with intermittent ejection of hot particles.

Dauerman and Tajima [3] studied the decomposition of nitrocellulose both separately and with

2% lead stearate additives. The additive caused an increase in the NO_3 concentration (although NO_3 was not directly observed) at burning-rate pressures as low as 10 torr, thereby increasing the oxidation potential of the reactions. The supporting experimental observations were: (1) an increased regression rate, (2) a higher overall chemical activity, and (3) an increased oxidation rate of C-H-O species by NO_3 and, possibly, by NO_2 . They thus determined that the increased regression rate was due to the faster rate of oxidation-reduction reactions induced by the lead catalyst.

A second conclusion based on their studies was that nitrogen dioxide apparently was not the initial decomposition product of solid double-base propellants. Furthermore, NO, rather than NO_2 , appeared to be formed when NO_3 was reduced, and NO_2 was not a primary product from decomposition of cellulose nitrate. They stated that Adams and Wiseman [13] had also made this determination earlier. Dauerman and Tajima further concluded that the predominance of nitric oxide as the volatized species indicated that NO_2 reacted very rapidly in the fizz, or precombustion, zone of nitrocellulose if it was indeed formed initially by rupture of the CO- NO_2 bond. NO_2 was complexed as the nitrate group (CONO₂) or was complexed immediately as it was formed when nitrocellulose was heated and then reacted very rapidly. This led to the formation of highly oxidized species such as H_2O , CO, CO_2 , and carbonyl and acidic intermediates.

Dauerman and Tajima [3] included a comment in their publication that the reviewers had suggested that their failure to observe NO_2 as the predominant species did not necessarily mean that the initial step was not a CO- NO_2 bond scission. The reviewer's argument was that the NO_2 formed would initially dissolve in the nitrocellulose and that oxidation processes leading to the reduction product NO would take place in the condensed phase. However, it should be noted that no attempt was made to determine the lead intermediates or any reactions involving the lead compounds.

Heller and Gordon [10] have concluded from gas-phase studies of double-base propellants that reactions between the nitric oxides and organic hydrocarbons occur in the foam and fizz zones.

Hewkin et al [4] proposed that plateau burning resulted from the lead-additive generating carbonaceous matter at or near the propellant surface. This in turn induced a reaction between NO and any of the reactant species in the vicinity, such as H₂, C, CO, and aldehydic moieties. However, if this were the mechanism, it would be anticipated that larger quantities of CO + CO₂ would appear in the final products since charcoal reacts with NO to form CO₂ + N₂.

Salooja [9] reported that whereas PbO inhibits the combustion of hydrocarbons, it strongly promotes the combustion of oxygen derivatives of hydrocarbons such as formaldehyde and acetates, thus increasing the formation of CO₂. Fifer and Lannon [8] also proposed that the Pb catalyzes the formation of CO₂ in the following reactions:



$$\Delta H = -41 \text{ kcal/mol};$$



$$\Delta H = -40 \text{ kcal/mol};$$



$$\Delta H = -89 \text{ kcal/mol}.$$

Since these are exothermic, they lead to higher temperatures. They are not in agreement with the theory of Camp et al. [11, 12] that the catalytic activity is located in the secondary flame zone. Rather, they suggest that catalysis takes place mainly in or on the burning surface, or in the fizz zone. They disagree with the chelate hypothesis on the basis that a nonchelate such as PbO can cause super-rate burning.

Kubota et al. [5] investigated various metallic, metal oxide, and metal organic additives to nitrocellulose and trimethylolethane nitrate (TMETN) propellants. The lead organic salt additives produced both super-rate and plateau burning. The regions directly affected by the lead compound were the condensed phase just below the burning surface and the burning surface itself (a distance of <100 μ at 1 atm and 20 μ at 20 atm), where the

lead compounds decomposed ultimately into finely divided metallic lead or lead oxide products. They proposed that the decomposition products of the lead catalyst reacted with nitrate esters in this surface reaction layer where the chemical degradation goes to NO₂, aldehydes, and so on, altering their normal thermal decomposition paths so as to produce an increased amount of carbon at the burning surface.

Kubota et al. [5] explained the plateau effect by theorizing that as the burning rate increased, the time available for the initial catalytic action in the surface reaction layer decreased. Thus the fraction of reactants affected by lead compounds and increased NO₂ decreased in the fizz zone with increased burning rate. That is, the super-rate burning diminished as pressure increased. With increased pressure the super-rate burning determined the slope of the burning-rate plateau.

This theory, however, differs from that of Hewkin et al. [4] who reported that carbon catalyzed the NO reduction in the fizz zone. Kubota et al. [5] stated that, instead, lead compounds increased the NO₂ concentration entering the fizz zone, which in turn accelerated the gas-phase reactions that utilize NO₂ as the oxidizer.

Suh et al. [6] investigated the addition of lead compounds to double base propellants and also found that imbedded thermocouples showed a hotter region at the surface of propellants containing lead salicylaldehyde or lead stannate. Their analysis of the gaseous products of combustion at 200 psi showed NO concentration to be reduced in all the modified propellants. They proposed that the lead modifier increased the burning rate in the lower region of pressure by expediting the initial decomposition reaction through the reduction of energy of either the RO-NO₂ or the R-ONO₂ bond. It was assumed that the lead in the modifier was in plumbous condition, where it formed a number of compounds. They suggested that the formation of the complex involving the nitro moiety weakened the RO-NO₂ bond, leading to an increase in the burning rate by expediting the dissociation of the nitrate ester. All of the lead salts that would thus modify the propellant, containing chelating compounds. Thus they concluded that the ballistic modifier

affected the initial step in the decomposition of NC propellants via an electronic interaction between the lead compound and NC.

EXPERIMENTAL APPARATUS AND PROCEDURES

The investigations were conducted in two different experimental systems. Phases 1 and 3 were performed in this laboratory's dual vacuum chamber-mass spectrometer apparatus. This system and the experimental procedures have been described previously [14-16]. Effusion cells were of alumina, with orifices of 1 mm diameter and 6.6 mm thickness. The cells had an inside diameter of 6.6 mm and length of 25 mm. The ion intensities were determined from their masses, isotopic distribution, and appearance potentials. Only the shutterable (i.e., chopped) portion of the ion intensities was directly recorded. Ion intensities used for equilibrium calculations were obtained with ionizing electrons 2 eV above their appearance potentials.

The combustion studies (phase 2) were conducted in the specially designed four-stage differentially pumped spectrometer system. Complete details of the experimental procedures and methods of calculation have been presented previously [17-21]. A molecular beam of frozen species formed in the flame at atmospheric pressure was sampled in the mass spectrometer at 10^{-9} atm pressure.

RESULTS

The mass-spectrometric investigation of the organic metallic salts and plateau burning propellants was conducted in three phases. The first phase was a decomposition study of several salts, including lead acetate, lead salicylate, lead resorcylate and copper salicylate. Manganese salicylate and silver salicylate were also tested. A covalent lead compound, tetraphenyl lead, was also investigated to determine its mode of decomposition or appearance in the low-temperature regions such as the fizz, or precombustion, zones. In the second phase lead and copper salicylate were added to an H_2/O_2 flame in the four-stage differentially pumped mass spectrometer apparatus to determine

their combustion products. The final phase concerned the investigation of the products of reaction at ignition of three propellants: (1) an ordinary double base propellant, (2) a double-base propellant containing 2.5% lead resorcylate, and (3) a double-base propellant containing 2.5% each copper salicylate and lead resorcylate.

Phase 1—Decomposition of Organic Metallic Salts

Decomposition of organic salts was studied in the effusion cells described in the previous section. Samples of 10-50 mg by weight were employed. The heating rate was controlled so that the pressure within the cell never exceeded that considered suitable for the molecular flow regime, 10^{-4} atm. This investigation did not include an attempt to obtain rate constants or other kinetic data.

Lead Acetate

Thermocouples inserted within the effusion cell were employed to record the temperature. Several hours were required for each experiment, during which time the temperature was raised gradually from ambient to approximately 1300-1400°C. The mass spectrometer sampled the effusion materials continually. At temperatures below 600-700°C only species related to the aliphatic or aromatic compounds were observed. The gaseous metal atom appeared above these temperatures. The continued mass-spectrometric sampling throughout the experiments produced numerous spectra. Several of these have been selected that effectively illustrate the type of results obtained. Figure 1 depicts a typical mass-spectrometric sampling of the effusing material as recorded at 410°C. The ordinate is the relative uncorrected ion intensity of the effusing species during decomposition. At this temperature the scan shows peaks attributable to the parent species of H_2 , H_2O , and CO_2 . The CO intensities are barely discernible above the noise level. As the temperature was increased to 550°C the CO peak became more pronounced but was still small compared to the CO_2 intensity. The OH radical, though not thermochemically stable at these temperatures, is produced from the pyrolysis of the salt. In the atomic mass unit (AMU) range 10-16 no peaks corresponding to CH , CH_2 , CH_3 , or CH_4 were seen.

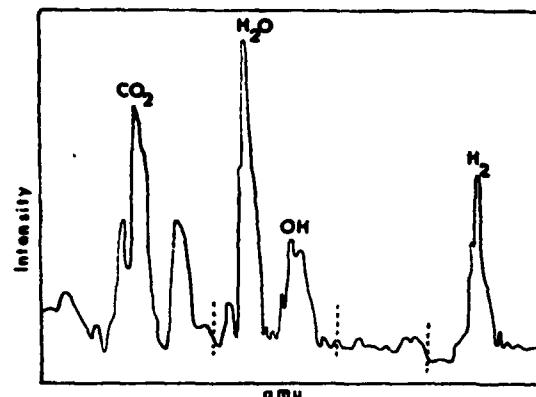
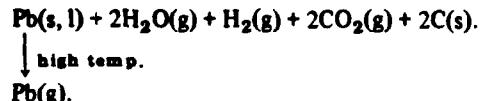
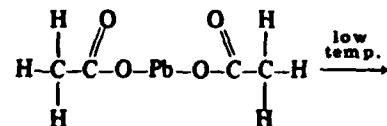


Fig. 1. Mass spectrum of the decomposition of lead acetate at 410°C in AMU range 0-50.

These species were depleted after several hours and were not observed at temperatures above 600°C. Time studies were made of the ion peaks, which did not remain at any constant value or ratio to other peaks during the decomposition time, indicating the decomposition to be kinetic. At 600°C the lead atoms were seen at fairly high intensities. Metallic lead has a vapor pressure of approximately 10^{-7} atm at 600°C. The mass-spectrometric sampling was continued until the temperature reached 1300°C. No other lead compounds were observed, although PbO, which has a boiling point of approximately 1300°C, would have been readily apparent if formed within the effusion cell. At the

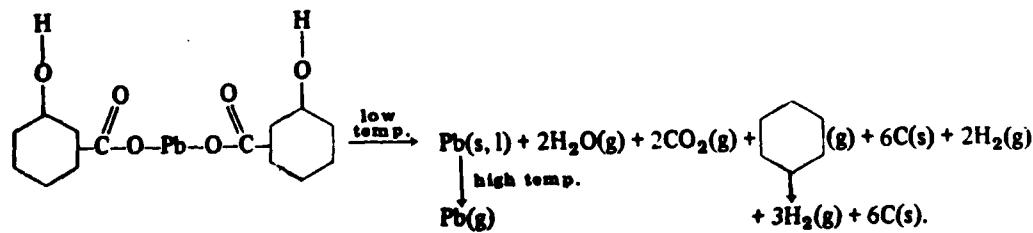
conclusion of the decomposition study the cell contents were examined and found to contain solidified lead droplets and solid carbon only. Since lead acetate does not contain enough oxygen to oxidize the carbon and hydrogen completely, it is not surprising that solid carbon was formed. Thus the overall decomposition of the lead acetate in the temperature range of 200-1000°C may be written as



This formula is merely a stoichiometric balance that fits the observed mass-spectrometric samplings and residual material remaining in the cell.

Lead Salicylate

Similar results were obtained with lead salicylate. However, a benzene peak appeared at low temperatures (<200°C). A probable mode of decomposition of the salicylate in two temperature ranges (low, 100-500°C; high, 500-1000°C) may be written as

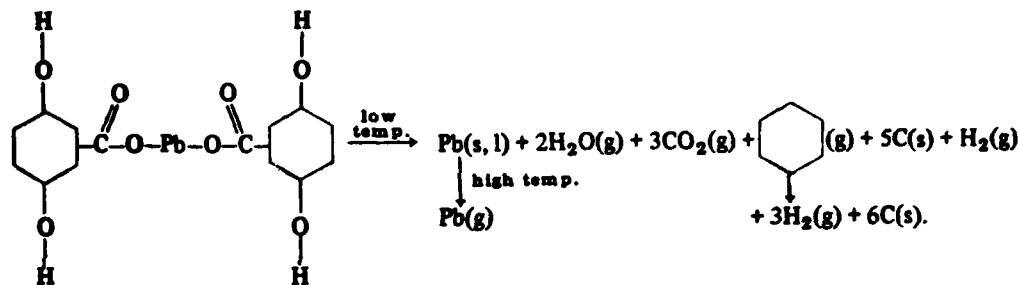


Lead Resorcylate

The results obtained with the decomposition of lead resorcylate were similar to those obtained with the lead salicylate. The decomposition follows the path of producing the stable compounds

H_2 , H_2O , and CO_2 , with some benzene appearing at temperatures below 200°C. As the temperature is increased the lead atom only appears, with no evidence of PbO or PbO_2 . The possible mode for the overall decomposition of the lead β -resorcylate

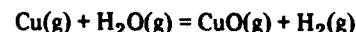
may be written as



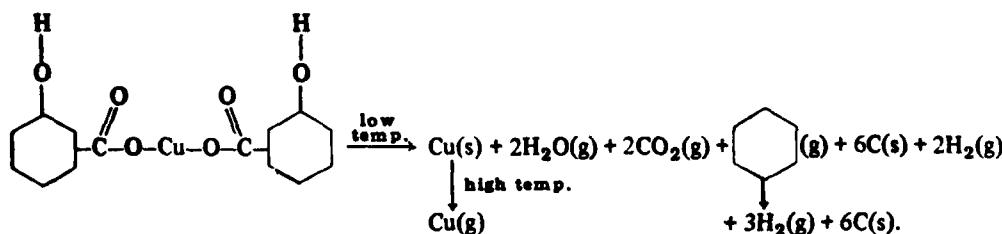
Copper Salicylate

The decomposition study of copper salicylate showed that, as in the case of the lead salts, the kinetic path of decomposition results in the formation of the stable species H_2 , H_2O , and CO_2 and gaseous Cu. Similar to lead salicylate studies, some benzene was noted at temperatures below 200°C. The species H_2 , H_2O , and CO_2 were observed below 500°C. Above 500°C no further decomposition products were observed until the metallic copper began to vaporize. At 800°C copper has a vapor pressure of approximately 10^{-10} atm. The Cu atoms were still observed at

1370°C, when the experiment was terminated. No $CuO(g)$ was seen at AMU 79. The free energy for the reaction of Cu and H_2O



at 1600 K is +28.8 kcal/mol. Thus the reaction to form gaseous CuO would not be thermodynamically feasible; however, it is likely that the condensed phase of $CuO(c)$ may occur. An examination of the cell contents disclosed some CuO and solid carbon. The probable mechanism for the thermal degradation of the copper salicylate is



Silver and Manganese Salicylate

The decomposition pattern of organic salts of manganese and silver was also studied, although these salts have not been successfully employed as plateau burning catalysts. The decomposition of silver salicylate followed the path of the lead and copper salts. However, in addition to metallic silver atoms, a small amount of AgO was seen in the mass spectrometer tracing at a temperature of 900°C. However, pyrolysis of manganese salicylate produced MnO in quantities nearly equal to those

of the Mn element. Neglecting the kinetics, and based only on thermodynamic considerations, it would be expected that the stability of $MnO(g)$ would be greater than that of $AgO(g)$. Brewer [22] lists the dissociation energy of AgO as 32 kcal/mol and of MnO as 95 kcal/mol.

Although the decomposition of the salicylates is chiefly kinetic, they are temperature-dependent. A study was made concerning the rate of evolution of H_2O from manganese salicylate in the temperature range 200–300°C over a 30-min period (see

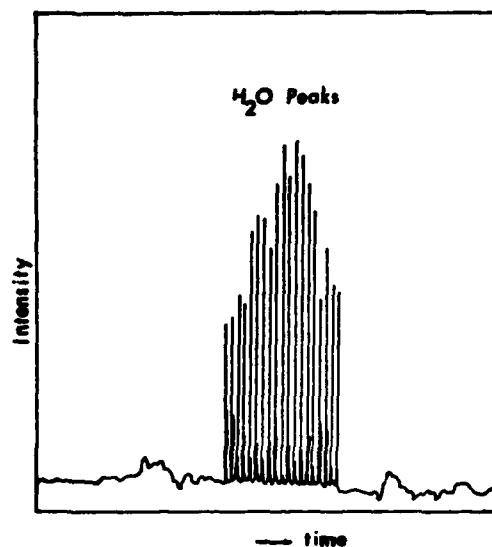


Fig. 2. Mass spectrum of the decomposition of manganese salicylate at 200-300°C showing the rate of evolution of H₂O for a 30-min. interval.

Fig. 2). As can be seen, during this period the evolution of H₂O increased nearly twofold with the rise in temperature. The H₂O concentration decreased during the last half of the period as the sample was depleted. This figure is illustrative of the time and temperature dependence of all the salts investigated.

Tetraphenyl Lead

Although most additive studies have involved metal organic salts of the type containing oxygen bonding to the metal, Suh et al. [6] also investigated a covalent lead compound, tetraphenyl lead, and found that all of the lead salts that modify the propellant in such a way as to cause super-rate or plateau burning contain chelating compounds. No evidence of plateau burning was found when tetraphenyl lead was added to the double-base propellant.

The results of the current investigation indicate that on heating tetraphenyl lead vaporizes without evidence of any decomposition. At temperatures of 400-600 K an effusion mass-spectrometric investigation showed tetraphenyl lead to vaporize without thermal decomposition. An apparent heat

of vaporization of approximately 40-50 kcal/mol was obtained from these vaporization studies.

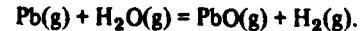
A fragmentation pattern at 40-eV ionizing energy was also made (see Fig. 3) over a lengthy AMU range (abscissa). The high ionizing energy ruptures the phenyl-lead bond and produces tri-, di-, and mono-phenyl lead, as well as metallic lead. Even with this high electron energy, rupturing of the phenyl ring was minimal. These results indicate that tetraphenyl lead is quite stable to thermal decomposition. The fact that tetraphenyl lead does not decompose to free the Pb atom may be the chief reason that it is not an effective additive for plateau burning propellants.

Phase 2-Combustion Studies of Lead and Copper Additives

This laboratory's four-stage differentially pumped molecular beam mass spectrometer apparatus described previously [17-21] was employed to study the combustion products of lead and copper additives.

Lead Salicylate

Although the low-temperature decomposition and pyrolysis studies showed the gaseous lead atoms available for reaction with the nitrate esters, their higher-temperature combustion showed the lead reacting with the various combustion species as determined by their thermochemical equilibria. Figure 4 shows the major peaks found during the combustion of lead salicylate at 2300 K. The species Pb, PbO, PbO₂, and H₃PbO₄ exist in nearly equal concentrations. The partial pressures obtained from the intensity measurements of the H₂/O₂ flame, corrected for ionization cross-sections and multiplier gain, were 0.5 atm and 0.005 atm for H₂O and H₂, respectively. The calculation methods have been described in detail in previous publications employing this apparatus [17-21]. Employing these values and the relative heights of the peaks in Fig. 4, a ΔG of 15.3 \pm 5 kcal/mol was calculated for the reaction



This results in a ΔH_{298} value of 12 \pm 5 kcal/mol

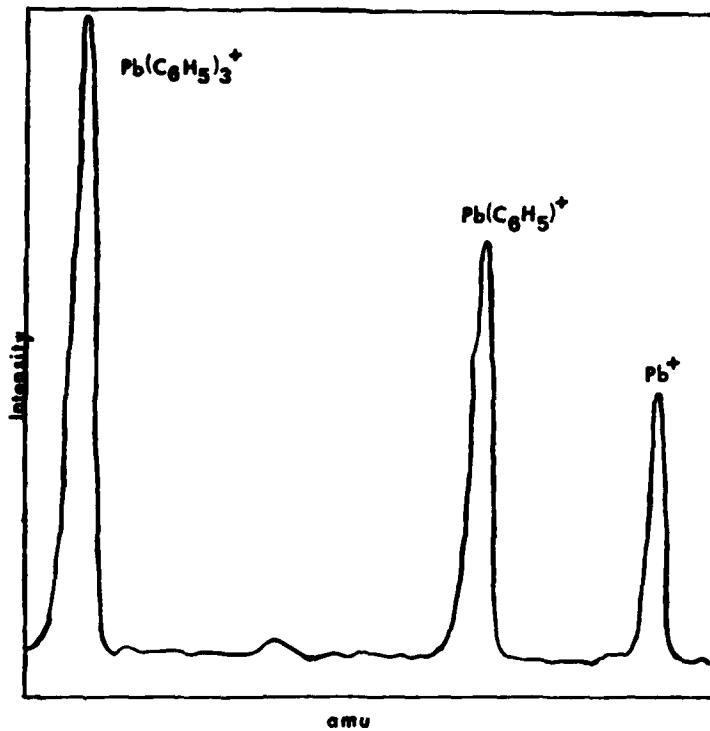
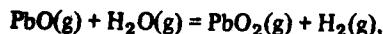


Fig. 3. Fragmentation pattern of tetraphenyl lead at an ionizing voltage of 40 eV at 500 K.

for PbO , which is in fairly good agreement with the reported value of 16 kcal/mol [23].

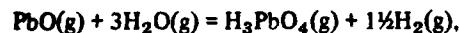
For the reaction



a ΔG of 16.5 kcal/mol was obtained. This results

in a ΔH_{f298} value of -24.5 ± 5 kcal/mol for $\text{PbO}_2(g)$.

For the reaction



a ΔG of 35.2 ± 5 kcal/mol was obtained at 2350 K. This results in a ΔH_{f298} of -62.3 ± 5 kcal/mol for $\text{H}_3\text{PbO}_4(g)$.

The reaction enthalpies would suggest that the final combustion products of the lead additives are those predicted by their thermodynamic equilibria.

Copper Salicylate

As in the case of the lead salicylate, high-temperature combustion (at 2300 K) of copper salicylate shows the formation of cupric oxide, cupric hydroxide, and gaseous copper atoms in nearly equal concentrations, as can be seen from the uncorrected ion intensities in Fig. 5. Free energies can be calculated for the reactions. A ΔG of 27.4

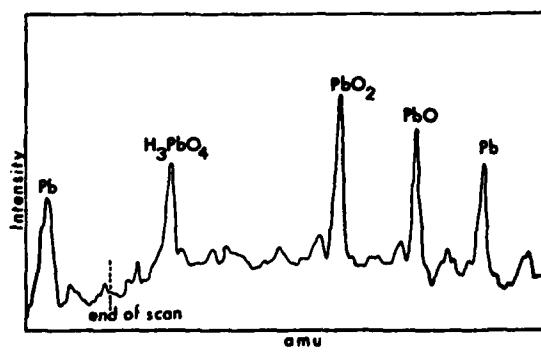


Fig. 4. Mass spectrum of the combustion of lead salicylate in the H_2/O_2 flame at 2300 K in AMU range 200-280.

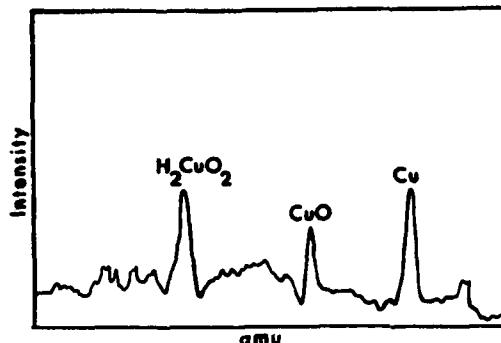
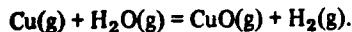
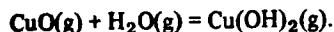


Fig. 5. Mass spectrum of the decomposition of copper salicylate in the H_2/O_2 flame at 2300 K in AMU range 50-100.

kcal/mol is calculated for the reaction



A ΔG of 0 is calculated for the reaction



Phase 3—Investigation of Ignition Products of Plateau Burning Propellants

The mass-spectrometric techniques described previously [14-16] were employed to study the reaction products of the plateau burning propellants at ignition. The propellant sample was placed in an effusion cell that was heated gradually until ignition occurred. The AMU range was monitored continuously to receive any species arriving from the ignition of the sample. The time-of-flight of a species within the quadrupole section is in the microsecond range. Previous studies at this laboratory measured species produced from electron bombardment in times of less than 100 ns (10^{-7} s) [24]. Thus the initial products formed in the propellant reaction can be identified if they effuse into the molecular beam to the mass spectrometer. Also, intermediate species having a short lifetime (on the order of milliseconds) would be receivable at the mass spectrometer.

Two plateau burning propellants were investigated. One contained 2.5% lead resorcylate, and the other contained 2.5% each copper salicylate and lead resorcylate. An ordinary double-base pro-

pellant without additives was also studied for comparison of the products of reaction. The propellants were double-base propellants containing approximately 50% nitrocellulose, 35-40% nitroglycerin, and small amounts of organic additives (including diethyl phthalate and nitrophenylamine) in addition to the abovementioned quantities of metal organic salts.

Ordinary Double Base Propellant

Mass-spectrometric studies were performed on a double-base propellant without additives at the ignition temperature ($\approx 200^\circ C$) to determine the first species arriving at the mass spectrometer as a result of ignition. The propellant was contained in a heated effusion cell, and the vapor species produced at the point of ignition were determined at fixed settings on the mass spectrometer. Samples of 1-2 mg were employed in these experiments. The mass spectrometer did not record any species prior to a sudden rise in pressure, which occurred at approximately $150-200^\circ C$. At this instant the species arriving at the mass spectrometer were presumed to be the ignition species, which then exited the cell within microseconds of ignition. Since the cell contained an elongated orifice, as previously described, a molecular beam was formed, allowing the species to enter the ionizing chamber of the mass spectrometer without further reaction after leaving the cell. The mass spectrometer was set on a specific AMU range so as to receive species, if any, having the same mass value. This procedure was employed since the cell pressure returned to normal vacuum (10^{-6} atm) within 1-2 s after ignition owing to the small quantity of propellant used. Figure 6 shows a composite mass-spectrometric tracing depicting several ignitions of the propellant at separate AMU settings. The intensities shown in Fig. 6 thus do not represent definite concentrations of gaseous species from any given propellant sample, but merely illustrate the species seen as a result of the ignition of an ordinary double-base propellant. This figure shows the H_2 , N_2 , CO , CO_2 , NO , NO_2 , and O_2 peaks. As can be seen, very strong CO_2 and NO_2 peaks are produced. Considerable amounts of H_2O are also present. From these mass-spectrometric ignition studies it appears that

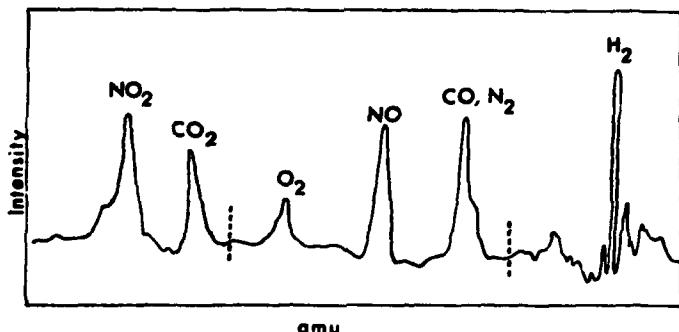


Fig. 6. Mass spectrum resulting from ignition of an ordinary double-base propellant at 180°C in AMU range 0-50.

the decomposition of double-base propellants produces a substantial quantity of NO_2 .

Following the ignition studies the combustion products of the propellant were examined. To produce the combustion products a larger quantity of propellant (≈ 20 mg) was introduced into the effusion cell. Since this quantity would take approximately 10 times longer to effuse from the cell, the temperature and pressure values within the cell had to be considerably higher than those employed when the sample was only 1-2 mg. Although these were not true steady-state combustion products, they sufficed to illustrate the effect of higher temperature and pressure on the combustion process.

Figure 7 shows the species from these experiments to be H_2O , N_2 , and CO_2 , with a small quantity of NO . The NO_2 concentration was negligible. Thus the mode of decomposition follows the initial breakup of the nitrate ester into NO and NO_2 groups, with a considerable quantity of molecular hydrogen; the subsequent combustion follows the equilibrium mode, producing the major species as predicted by the thermodynamic equilibria.

Lead Additive Double-Base Propellant

For the investigation of the plateau burning double-base propellant containing 2.5% lead resorcylate the mass spectrometer was set to receive species in the AMU range of 200-300, which would include Pb intermediates or compounds. The effusion cell was gradually heated until a pressure change was noted on the ionization gauge, indicating a release of gaseous material. After ignition, but prior to combustion, gaseous atomic Pb and PbNO_2 were observed in the mass spectrometer. Figure 8 shows a noise level in the 200-300 AMU range as the cell was being heated and the Pb and PbNO_2 arriving at the mass spectrometer following ignition.

Other propellant species produced were also identified. Figure 9 shows the major vapor species present after ignition. The mass range 15-18 AMU depicts the H_2O , OH , and CH_3 peaks, 24-32 AMU the C_2H_2 , CO , N_2 , NO , and O_2 peaks, and 44-46 AMU the CO_2 and NO_2 peaks.

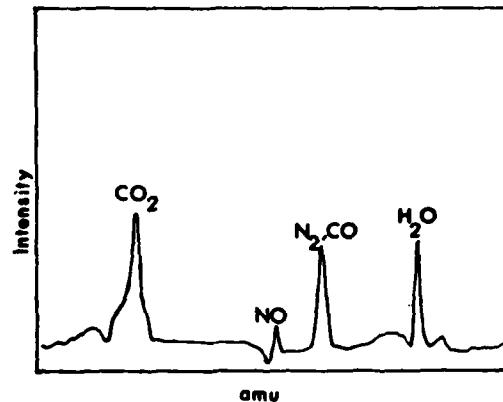


Fig. 7. Mass spectrum showing the major flame species of an ordinary double-base propellant in AMU range 15-50.

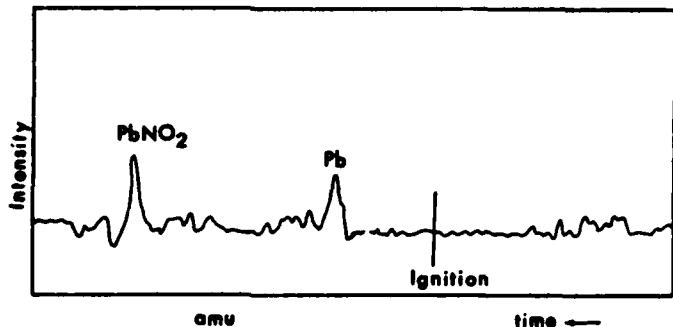


Fig. 8. Mass spectrum of the lead additive double-base propellant at ignition in AMU range 200-275.

Copper and Lead Additive Double-Base Propellant

A double-base propellant containing approximately 2.5% each of lead β -resorcylate and cupric salicylate was also investigated.

Initially, ignition studies were conducted, with the mass spectrometer set to cover the AMU range 60-130 to determine the species Cu, CuO, CuOH, CuNO, CuNO₂, and CuNO₃, if present at ignition. The propellant was heated gradually in an effusion cell until ignition occurred. Repeated runs were made at the various AMU peaks to determine whether any Cu species were present. Figure 10 is

a composite oscilloscope tracing depicting the functioning of the mass spectrometer before and after ignition. The Cu(g) species appears at ignition. As can be seen, no peaks are present in the AMU range 70-110 until a peak at 110 corresponding to CuNO₂(g) is observed. No oxides or hydroxides are discernible above the noise level. Figure 8 shows similar Pb and PbNO₂ peaks from this propellant.

DISCUSSION

Examination of the results of the three-phase investigation provided some insight into the aspects

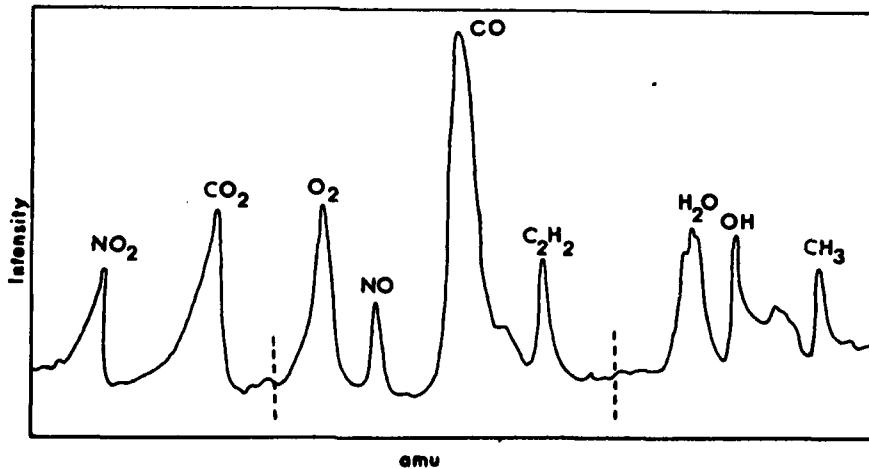


Fig. 9. Mass spectrum of a lead additive double-base propellant showing species released at ignition in AMU range 15-50.

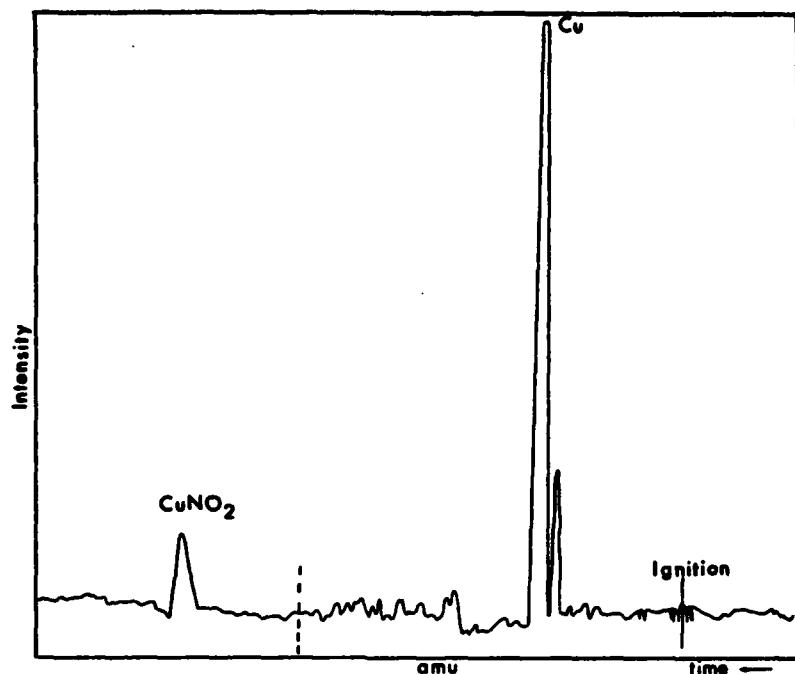


Fig. 10. Mass spectrum before and after ignition of a copper and lead additive double-base propellant in AMU range 50-110.

of plateau burning propellants. From the review of the previous studies noted in the "Background" section, it is readily apparent that the proposed theories are conflicting; thus the present results agree with some and disagree with others. In this regard, an attempt has been made to assess the significance of the results obtained in this study.

Phase 1—Metal Organic Salt Decomposition

Several important facts were ascertained from these experiments, including:

1. The lead and copper acetates, salicylates and resorcylates do not vaporize, but decompose.
2. One of the primary purposes was to determine what metallic species were formed as a result of the decomposition of the organic salt. No lead or copper vapor species, with the exception of $Pb(g)$ and $Cu(g)$, were observed at temperatures up to 1400°C. The boiling point of PbO is 1300°C; therefore, if the PbO species were present, it would have been readily observed. The only metallic oxides observed were from the decomposition

of the silver and manganese salicylates. However, these salts are not known to have been previously employed in propellant compositions.

3. The materials remaining in the cell after completion of a decomposition experiment on the lead organic salts over several hours were solidified metallic droplets and carbon. The formation of the droplets agrees with the results of the propellant investigations of Preckel [1] and Camp et al. [11, 12]. Preckel made photomicrographs of the burning propellant surfaces and the sloughed off carbonaceous debris during strand burning tests in a closed bomb. Globules of molten lead were observed at all pressures below the upper limit of the plateau but did not appear above the plateau limit. Camp et al. [11, 12] presented a condensed-phase hypothesis, proposing that the absorption of radiation below the burning surface of the propellant is a significant factor in super-rate burning. Their explanation was that the plateau burning phenomenon is produced as a result of the formation of agglomerated globules of lead metal

on the burning surface that shield the surface from absorbing radiation. They also suggest that the accumulation of lead metal on the surface increases with pressure.

4. The metallic bonding in the Pb and Cu salts is apparently weak in comparison to that of the C-O or H-O bonding, resulting in release of the free metal in the solid and liquid phases. On further heating, whether by radiation or directly, the metal atoms vaporize.

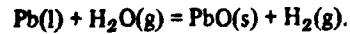
5. The major additive Pb and Cu salicylates and resorcylates are low in oxygen content and decompose with the formation of solid carbon.

6. Tetraphenyl lead did not decompose, but vaporized. This result is significant since previous propellant studies by Suh et al. [6] showed that this additive did not produce a plateau effect. They attributed this to the covalent bonding of the tetraphenyl lead. However, since our studies show that the tetraphenyl lead remains intact, it evidently does not enter into reaction with the organic decomposition products in the precombustion phase, thus having the effect of an inert additive. At flame temperatures above 2000°C the tetraphenyl lead is consumed in the same manner as the other metallic additives.

Phase 2—Combustion of Metal Organic Salts

The combustion products of the metal organic additives are those predicted by thermodynamic equilibrium calculations. The oxides and hydroxides of lead and copper release energy on their formation and thus would increase the heating value of the plateau propellants, as found by other investigators [2, 5, 6].

The observation of metallic oxides and hydroxides in the combustion phase but not in the heating of the organic salts cannot be directly compared since the salt decomposition is kinetic, whereas the formation of the oxides in the flame is thermochemical. However, the free energies do not favor the formation of PbO(s) at low temperatures from the reaction



At 700 K the ΔG is 17.0 kcal/mol employing

JANAF Table data [23], indicating the stability of elemental lead in comparison to the lead oxide. At the combustion temperature of 2300 K the thermochemical calculations employing JANAF data predict the ratio of Pb(g)/PbO(g) to be nearly unity, which is in agreement with the relative peak heights shown in Fig. 4.

Phase 3—Ignition of Plateau Burning Propellant

Immediately on ignition each sample of ordinary double-base propellant was found to produce NO₂. However, the combustion products of this propellant showed only minor amounts of NO₂. These results agree with those of Preckel [1] and Kubota et al. [5], who studied the mechanism for nitrate decomposition to NO₂. Dauerman and Tajima [3] also observed NO₂, although they felt that it had arrived from NO₃. Adams and Wiseman [13] also suggested that NO₂ resulted from NO₃ reduction. In the current studies of the double-base propellants there was also no observation of NO₃(g), although the mass spectrometer was set at AMU 62 to record the NO₃⁺ ion if NO₃(g) entered the ion source. Since kinetic studies have shown that the NO₃ species has a lifetime of approximately 3 s [25], it would have been easily observable if produced. The current results support the cleavage of the CONO₂ groupings into CO and NO₂ instead of NO₃ as suggested by Dauerman and Tajima [3].

The phase 1 studies indicate a stripping of the organic material from the metal atom, while the propellant decomposition data indicate that at ignition and prior to reaching the adiabatic combustion temperature hydrocarbons and NO₂ are produced. Therefore, it is considered possible that the free metallic gaseous atoms are available for reaction with the NO₂ produced from the nitrate ester decomposition. The free energy of reaction would favor the formation of PbNO₂ from the combination of Pb(g) and NO₂(g). The stripping of the organic material from the lead atoms would also produce Pb droplets, as predicted by Camp et al. [11, 12]. However, investigation of the role that these might play in the plateau burning phenomenon is not a part of the current study, since the study was made entirely of gas-phase species,

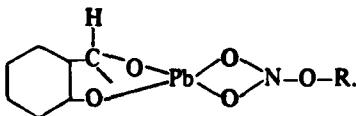
whether occurring from reactions on the burning surface, fizz zone, or in the combustion area.

The following observations based on the results of the three-phase study of the chemistry involved in gaseous reactions support the conclusion that formation of the metallic nitrite is a possible explanation for the plateau effect: (1) PbNO_2 is formed on ignition of the propellant; (2) the reaction of $\text{Pb}(\text{g})$ with $\text{NO}_2(\text{g})$ may cause additional stripping of NO_2 from the ester, causing the higher burning rate. (this phenomenon has also been predicted by Kubota et al. [5] and Suh et al. [6]; (3) only Pb , PbO , PbO_2 , and H_3PbO_4 were found in the combustion equilibrium products.

These conclusions based on the current studies agree with only some of the previous investigations. For example, the results do not agree with Preckel's hypothesis [1] in which Pb reduces NO catalytically as



since $\text{PbNO}_2(\text{g})$ was observed. However, the current work agrees with the hypothesis of Suh et al. [6] that the tying up of the NO_2 species in some way with the lead moiety is a cause for the super-rate burning by expediting the dissociation of the nitrate ester, but it does not agree with their suggested mechanism in the formation of a complex between the chelate, a lead atom, and alkyl nitrate, possibly structured as



Several previous plateau burning experimental programs have suggested that PbO is an effective catalyst [4, 26]; however, Kubota et al. [5] did not find this to be the case. The current studies appear to support the necessity of the Pb atom for the catalytic effect. In this case, where carbon is present, it will reduce the PbO as



freeing the Pb atom for the catalytic effect.

Hewkin et al. [4], found that Fe_2O_3 , Co_2O_3 , CuO , ZnO , SnO_2 , and Al_2O_3 increased the burning rate with pressure. However, PbO was the only metal oxide to produce super-rate and plateau burning. Their results agree with those of the current investigation that it is necessary to produce the metallic atom. The oxides that Hewkin et al. [4] studied would not decompose to yield the metallic atom at fizz zone temperatures. Even metal organics that do not decompose, such as tetraphenyl lead, are not catalytic.

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